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Vol. III - Wastewater Treatment

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16. ABSTRACT

This study has surveyed the military explosives and propellant manufacturing industry, covering both "GOGO" and "GOCO" facilities. Sources of wastewater, volumes, and pollutant constituents have been reported where such data existed.

Treatment technology currently in use at the various installations has been described, including effectiveness of pollutant removal and secondary (air and solid) waste generation. Systems under development at these military installations have also been examined and evaluated in light of available information.

The report consists of three volumes. Volume I presents general conclusions and recommendations and describes the industry's manufacturing operations. Volume II presents the bulk of the data concerning the wastewaters and the treatment systems now in place. Volume III reviews and summarizes data from the first two volumes and describes and evaluates the new treatment processes under development at this time.

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STATE-OF-THE-ART: MILITARY EXPLOSIVES AND PROPELLANTS PRODUCTION INDUSTRY

VOLUME III WASTEWATER TREATMENT

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This project, "State-of-the-Art: Military Explosives and Propellants Production Industry", was undertaken as part of Environmental Protection Agency's Miscellaneous Chemical Industries program to establish a baseline of information concerning the military explosives industry, the magnitude of its waste problems, and the adequacy of the industry's treatment technology. The results of the study have indicated that many of the wastes do present significant problems of toxicity and/or resistance to treatment, in addition to problems unique to explosives. Although some treatment systems in use do protect the nation's waterways from contamination, others are inadequate, generate secondary air or solid waste problems, or are not widely used due to budgetary limitations. Further research effort is needed by EPA and/or Department of Defense to control pollutants generated by certain sectors of the industry. The data and results of the investigation have been used extensively by EPA's Office of Water Programs in developing standards for the explosives industry. It will also allow engineering staffs at several commercial military manufacturing facilities to examine their wastes and compare control technology with that being used or developed at other installations. Finally, it will enable EPA to determine our own research efforts in this industry and how they would relate to other programs. Questions or requests for additional information should be directed to the Industrial Environmental Research Laboratory - Cincinnati, Field Station - Edison, New Jersey.

David G. Stephan
Director
Industrial Environmental Research Laboratory

ABSTRACT

This study, contained in three volumes, addresses the wastewater effluents of the military explosives and propellants production industry. Both manufacturing and LAP (Load, Assemble, and Pack) activities are covered. Volume I describes the industry, as well as the production processes and technology. Volume II details the wastewater effluents of manufacture and LAP operations by product, process, and military installation, to the extent that data are available. Volume III describes and evaluates the effectiveness of various treatment technologies for water pollution abatement now in use or under investigation by product, process, and military installation.

A comprehensive long-term effort has been underway by the Department of Defense for a number of years for the purpose of modernizing munitions production plants. Pollution abatement is an integral part of the modernization program. Although extensive study, research and development investigations have been undertaken, and although significant water pollution abatement and water management plans have been developed, implementation is generally in only the initial stages at selected military facilities. Major Government emphasis and very substantial funding are essential to: the continuation of necessary pollution abatement research and development; the demonstration of promising new treatment technologies; and the implementation of effective and economical treatment system construction programs. Recommendations are set forth in detail in Volume I.

VOLUME III

CHAPTER VI

WASTEWATER TREATMENT

The reader of this report is advised that it consists of six chapters, contained in three volumes, each addressing separate aspects of the explosives and propellants wastewater effluents and treatment situation, and that duplication and repetition among these chapters has been kept to a minimum. Thus, the reader is cautioned that the use or interpretation of statement or evaluations taken out of context from the study in its entirety could lead to serious misunderstandings and incorrect assessments.

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CHAPTER VI

SECTION I - INTRODUCTION

1. This chapter is devoted to: an evaluation of current treatment technologies applied to manufacturing and LAP wastewaters associated with military explosives and propellants; an assessment of the effectiveness of current methods of treatment as well as those under development; and an identification of alternate treatment procedures which might: (1) be applicable where none are now in use; (2) be more effective than those now in use; or (3) provide the opportunity for recovery of materials currently discharged without treatment or lost through treatment.

a. The conclusions and recommendations resulting from the evaluations made in this Chapter are summarized in Chapter I, Volume I.

b. The chapter is divided into nine principal sections as follows:

I. Introduction
II. Trinitrotoluene
IIA. Red Water
IIB. Pink Water/LAP
III. Acids
IIIA. Acetic Acid and Acetic Anhydride
IIIB. Nitric Acid Manufacture and Concentration
IIIC. Sulfuric Acid Manufacture, Concentration and Recovery
IV. Nitrocellulose
V. RDX and HMX
VI. Nitroglycerin
VII. Sellite
VIII. Propellants
IX. Miscellaneous LAP Activities
IXA. Cast Propellants
IXB. Cast Explosives
IXC. PBX

c. Each Section briefly describes pertinent product manufacturing or handling procedures, and, to the extent that information is available, identifies significant waste sources, and wastewater volumes and characteristics. This is followed by a discussion of water management techniques, where significant reductions in waste volume, or product recovery by process modifications appear feasible. Thereafter, each section describes and evaluates current wastewater treatment practices and modifications to current treatment practices under development. The next major sub-section is devoted to an evaluation of the applicability of alternative treatment technologies, beyond those currently in use or proposed. Where current or projected air pollution abatement procedures are expected to impact on wastewater volumes or characteristics, the impact of air pollution control is also discussed. Finally, each section closes with a brief summary.

d. The conclusions and recommendations resulting from the evaluations of treatment technologies currently in use or under development are presented in Chapter I, Volume I.

e. The contents of the preceding two volumes are as follows:

(1) Volume I. Introduction to The Military Explosives and Propellants Industry. Executive Summary, Conclusions and Recommendations.

(2) Volume II. Characterization of The Wastewater Effluents of The Military Explosives and Propellants Industry, including Detailed Data Tables.

f. The evaluations of treatment technology presented in Chapter VI (Volume III), as well as the conclusions presented in Chapter I (Volume I) are based upon a wide range of data, data collection methods, data collection conditions and analytical procedures, as well as a wide variety of data sources, many of which are incomplete, and some of which are conflicting. As a result, the conclusions and recommendations assessing the effectiveness of treatment technologies represent the best professional judgments of the authors, within the constraints and limitations of available factual data. In some instances, lack of data in published form on current investigations have precluded incorporation of an adequate assessment of these investigations. Data sources are cited in detail throughout Chapter VI, and are listed in Appendix 1, "References."

g. The evaluations presented in Vol. III are based upon the most recent information available at the time of final editing of this Report. Data in Vol. III may be in conflict with data presented in Vol. II, which are based primarily on AEHA monitoring and survey studies, some of which are several years old.

SECTION II - TRINITROTOLUENE

2. Introduction

There are three basic wastewaters associated with the manufacture and loading of TNT into munitions. These are: spent acids and acid washes; red water; and pink water. Red water results from the sellite purification step in TNT manufacture. Acidic wastes result from the toluene nitration steps. Pink water results from TNT contact with plant clean-up and scrubber water during manufacturing and LAP operations, and as a condensate from red water evaporative concentration and incineration.

Pollution abatement for acidic wastes will be discussed separately in Section III of this chapter, since acid wastes are characteristic of many products, including TNT, nitroglycerin and nitrocellulose.

SECTION II-A - RED WATER

3. Waste Sources

a. The purification process in TNT manufacture entails the use of sellite, a concentrated (16%) solution of sodium sulfite (Na_2SO_3). Crude TNT is washed with sellite and the unwanted isomers of TNT react with it, leaving α-TNT. The sellite solution, together with subsequent rinse waters, constitutes the red water. Currently, some TNT manufacturing plants have a market for this red water in the paper industry. However, the market is only a short-term solution to the disposal of red water, since the paper industry through process modifications will eventually negate the need for red water. Thus, the Army must become independent of an outside market, insofar as the disposal of red water is concerned.

b. Several approaches have been investigated to treat the red water generated in the sellite TNT purification step:

(1) Evaporative concentration and/or incineration of red water.

(2) Regeneration of sellite precursors from red water liquor or ash by either the fluidized bed reduction technique or "Tampella" process.

(3) Carbon adsorption to remove the organic constituents of the red water.

(4) Flocculation and filtration to remove the color material by proper coagulants and coagulant aids.

(5) Acidification of the red water to recover the nitrobodies for reuse in making TNT.

Approach 1 above is currently used to concentrate red water prior to sale to the paper industry and, where there is no market, to convert the red water to dry ash for land disposal. Red water incineration has been practiced at Joliet, Radford and Volunteer AAP's. Newport AAP, now undergoing reconstruction for modernization, will also utilize red water incineration if necessary. The remainder of the approaches described above are under investigation as potential replacements for incineration.

c. The incineration ash contains as its major components sodium sulfate (79 percent) sodium carbonate (14 percent) and sodium sulfite (4 percent). Ash production at the modernized Newport AAP is projected at 1500 lbs/hour at a TNT production rate of 15 million lb/month (3f). The evaporation condensate, while essentially distilled water, contains sufficient nitrobody color to be classified as pink water. Data from Joliet AAP show the nitrobody content of the condensate to be about 15 mg/l (3f). Color development occurs at TNT levels as low as 1.5 mg/l, while α-TNT is soluble up to 200 mg/l (3i).

d. Crude TNT purification by sellite washing removes selectively the three to five percent of unwanted TNT isomers containing a nitro group in the three or five position. In the modernized continuous TNT lines, the sellite wash (red) water contains about 25 percent dissolved solids. Typically, this might include 17.3 percent organics, 2.3 percent sodium sulfite, 0.6 percent sodium sulfate, 3.5 percent sodium nitrite and 1.7 percent sodium nitrate (15zp). Red water from the older, batch process is more dilute, but represents about 1.6 times the mass of impurities per ton of crude TNT manufactured by the continuous process (15zp). The batch process red water normally contains residual spent nitrating acids, which in the continuous process are washed out separately. In the continuous process, water wash of the TNT, yielding "yellow water" then precedes the sellite wash. This water wash removes the residual acidity and the resulting yellow water contains nitric and sulfuric acids plus nitrobodies. Schulte, et al. (16h) have reported that the production of 100 lbs of TNT by the continuous process requires 47 lbs toluene, 210 lbs sulfuric and 125 lbs nitric acids, 6 lbs sodium sulfite, 1 lb soda ash and 640 lbs water. The resulting waste volume is about 100 gallons.

e. There are considerable differences in both the waste volume and character between the batch and continuous TNT processes. For example, in the batch process there is a neutralization wash with soda ash solution, prior to the sellite wash (1g(3)). This is not used in the continuous process. Instead, a water wash precedes the sellite wash and this acidic "yellow water" is returned into the toluene mono-or dinitration step. The acid wash is then followed by two sellite washes. The result of this modification is both a reduction in wastewater volume, and reduced discharge of constituents associated with the batch neutralizing wash. Excess yellow water, above that volume that can be returned to the nitration stages, is combined with other process wastes for treatment by either incineration or neutralization (3f). It has been reported, for example, that at Radford AAP the total process water use is 240 gal/ton

TNT (3u). Of this, 22 gal/ton is yellow water which is returned to the continuous nitration line, and 106 gal/ton is red water from the sellite wash. The balance is scrubber water.

4. Effects of Water Management

a. As a result of various water management programs, particularly those associated with the continuous TNT manufacturing process, waste streams will be both reduced in volume and segregated according to their character. For example, Radford AAP proposes to reduce process wastewater discharge from each of their continuous lines from 53,000 down to 8,500 gpd (3za). This reduction will result from: reducing the number of wet scrubbers required for acid fume control; return of acidic yellow water to the first or second nitration steps; recycle of transfer water between TNT purification and finishing stages and other recycle flows. After implementation of these water management programs, the TNT lines will have a tank car wash water flow of 15,000 gpd, which will be recycled (3za). In addition, an estimated 4,200 gpd of red water per TNT line (84 gal/ton) will be sold off-plant, or disposed of by incinerator (3za). The incinerator will also receive excess yellow water, after neutralization and blending with red water, and water from the post-nitration acid wash (1n(3), 15x).

5. Current Treatment Practice

a. Red water resulting from sellite purification is first concentrated in rotary kilns to about 35-40 percent solids (3f). The concentrated liquid is then either sold to the paper industry, or incinerated to a dry residue. This technique was reported by Schott, et al. in 1943 (16i) and patented by Hales, et al. in 1945, as a method to avoid violent ignition of the residue (16j). It remains the only proven method for disposal of large quantities of red water (16k).

b. At Radford AAP, ash residue from red water incineration was disposed of to a sanitary landfill from 1969 through 1971 (3f). Thereafter, the red water was concentrated and sold (1n(3)). The red water incinerator consisted of four single-chamber rotary kilns. A reported 24,000 tons of red water were incinerated per year, using natural gas at 700,000 ft^3 per month as the primary fuel (4c). The ash yield was 90 tons per year. Joliet AAP stockpiles red water incinerator residue on open land. It has been reported that at Joliet AAP, 0.179 lbs of ash is produced per lb of TNT manufactured (1g(3)). Approximately 200 million pounds of ash are now stockpiled. The residue is reported to be 90 percent soluble, and some is washed away by rainwater (15zb). The red water disposal plant, built in 1965 at a cost of $8 million, uses fuel oil.

c. The Volunteer AAP red water incinerator complex utilizes twelve rotary kilns to incinerate red water produced in excess of that sold to the paper industry. Newport AAP, out of production while the plant undergoes modernization, will continue to use rotary kilns, as in the past. Pink and yellow water streams will be neutralized, concentrated and blended with red water for incineration disposal. Ash production at the modernized plant is estimated at 1500 lbs/hour, at a TNT production rate of 15.0 million lb/month. Ash will be landfilled, with the landfill sites lined with protective membranes to prevent ground water contamination (3f). It has also been reported that water runoff from the ash pile will be collected and lime-treated (3f). This is presumably intended to partially control sulfate discharge by precipitation of gypsum.

d. In each plant, the evaporation condensate represents a disposal problem. The condensate contains sufficient nitrobody color to be classified as pink water. For example, condensate from the Joliet AAP has a typical nitrobody content of 15 mg/l. In no instance is this condensate treated before discharge. The potential treatment technology applicable to this condensate will be discussed in a subsequent section of this chapter.

e. The existing evaporation/incineration treatment process suffers from four deficiencies: (1) the condensate does not comply with accepted standards for nitrobody content; (2) energy requirements for red water concentration and incineration are high; (3) the ash residue presents a major solids disposal problem, with significant potential for surface and groundwater contamination; and (4) there is a potential air pollution problem associated with the incinerator operation. The U. S. EPA has reported 50 tons per year particulate matter, 5 tons per year SO_x and 648 tons per year NO_x emitted from the Radford AAP red water incinerator (4c).

6. Modifications to Current Treatment

a. Because of the deficiencies of the present red water disposal program, the Army currently has under investigation several modifications. Modifications which have or are being studied include: (1) reverse osmosis as the red water concentration step prior to incineration, and to recover recycle water; (2) red water acidification to remove one sulfonate group from the TNT isomers, and allow recycle of DNT into the nitration process or the recovery of useful products such as diaminotoluenes; (3) a fluidized bed reduction system to recover useful by-products from the incinerator ash; and (4) the "Tampella process" which would recover useful products directly from the red water.

b. Concentration of the red water by reverse osmosis has been studied at Volunteer AAP, using a two-stage pilot unit. Pretreatment with sulfuric acid was required to lower the pH from above 8 to 7 or below, in order to prevent scale formation in the RO unit. Pilot tests indicated that direct concentration of red water from 5 percent to the 35 percent strength required for incineration, was impractical. The RO unit could concentrate to 14-15 percent solids, although significant leakage of TNT through the RO membrane occurred (3h, 3i). Reverse osmosis thus appears impractical, except as a water recovery step, followed by further concentration in evaporators.

c. The red water acidification process is aimed at desulfonation, and recovery of DNT (3h). Unsuccessful attempts were made at Radford AAP to desulfonate 2,4- dinitrotoluene-5-sulfonic acid, and additional efforts are planned (15zp). Figure 1 is a concept schematic for a complete recycle acidification process. The process depends, however, upon a development of capability to successfully produce DNT in the hydrolysis reaction.

d. The fluidized bed reduction system involves a chemical conversion of red water incineration ash. The ash is ground for optimum fluidization, and is reacted with a reducing gas which at the same time is used to fluidize the solids. Water and CO_2 are added to carbonate the reduced products. The products expected from the process are Na_2CO_3 and H_2S, which can then be used to remanufacture sellite, thus recycling the wastes. A process schematic is shown in Figure 2. The reducing gases are H_2 and CO, in N_2 (3h). A technically feasible fluidized bed process has recently been investigated at bench scale level (3z). However, problems with maintaining fluidization at high temperatures and slow second order kinetics have resulted in abandonment of the process (15zp).

e. The most promising process appears to be the Tampella process, which has been successfully used in the paper industry (3f). The Tampella process uses the concentrated red water liquor, in a reduction atmosphere, to also produce Na_2S which can be carbonated to yield Na_2CO_3 and H_2S, which can then be recycled to produce sellite. The initial pilot work on this process has been completed, and proved successful. Further study is required to assess the effect of impurities and process economics (15y). Investigation of alternate concentration procedures is warranted.

7. Alternatives to Current Practice

a. Alternative treatment technologies considered for red water include: (1) activated carbon; and (2) chemical destruction. A limited amount of work has been carried on with each of these technologies.

b. Schott, et al. (16i) reported in an early study of red water that activated carbon dosages up to 2000 mg/l (8.34 tons carbon/MG* red water) produced only 15.8-36.5 percent reduction in the organic content of the waste, while even higher dosages (up to 10 gm/l) were required for effective color removal. The authors concluded that activated carbon treatment, although somewhat effective, requires excessive quantities of carbon and would be prohibitive in cost.

c. In a later, and more extensive study of carbon treatment of red water, Schultz, et al. (16h) reported that in addition to TNT, other compounds present in the red water, (some formed by side reactions in the sellite purification step), include hexanitrodibenzyl, tetranitromethane, cyanic acid, trinitro benzoic acid, dinitrocresol, phenol and various nitrotoluene sulfonic acids. In their carbon work, they studied the treatability of red water from a continuous TNT line.

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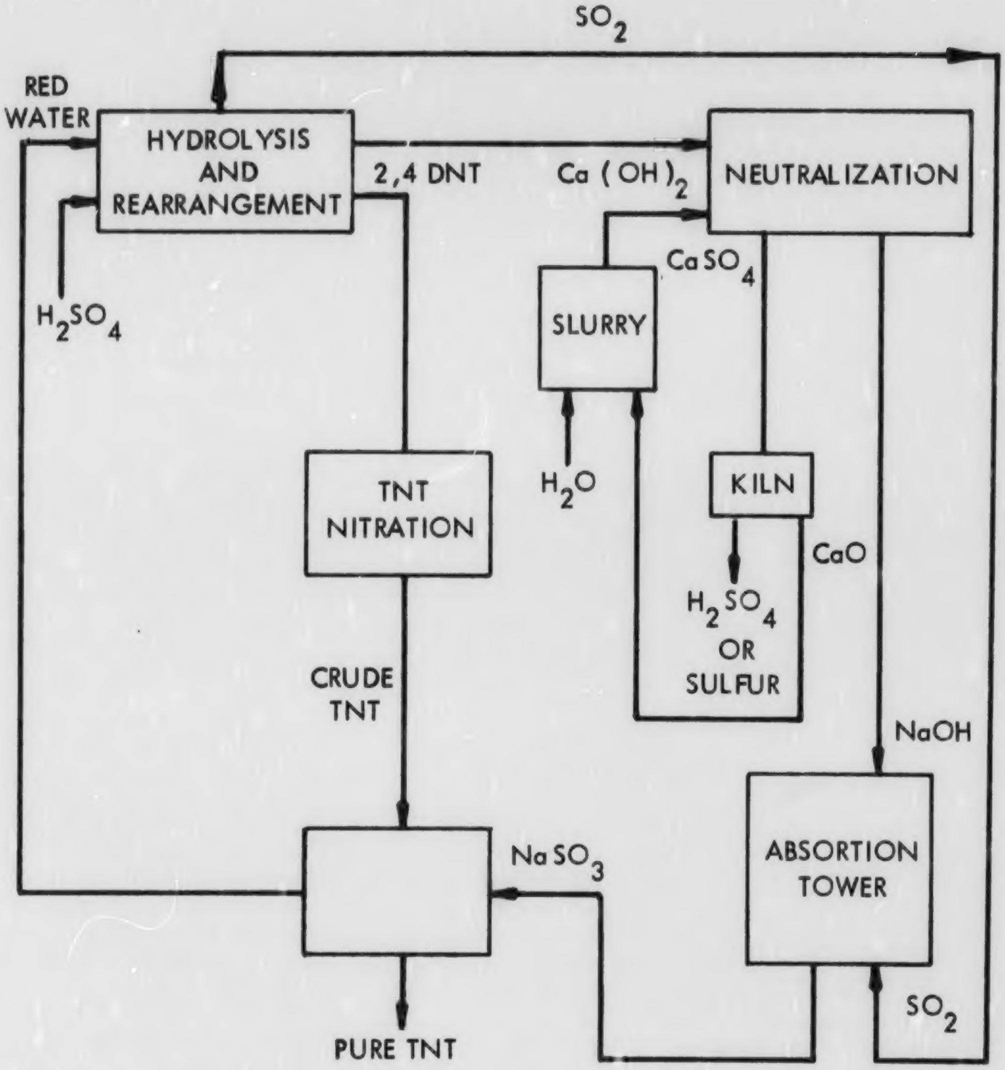
*MG = million gallons



SO_2
RED WATER
HYDROLYSIS AND REARRANGEMENT
2,4 DNT
$Ca(OH)_2$
NEUTRALIZATION
H_2SO_4
$CaSO_4$
SLURRY
TNT NITRATION
H_2O
KILN
CaO
H_2SO_4 OR SULFUR
CRUDE TNT
NaOH
$NaSO_3$
ABSORTION TOWER
SO_2
PURE TNT

Figure 1 - Acidification of Red Water

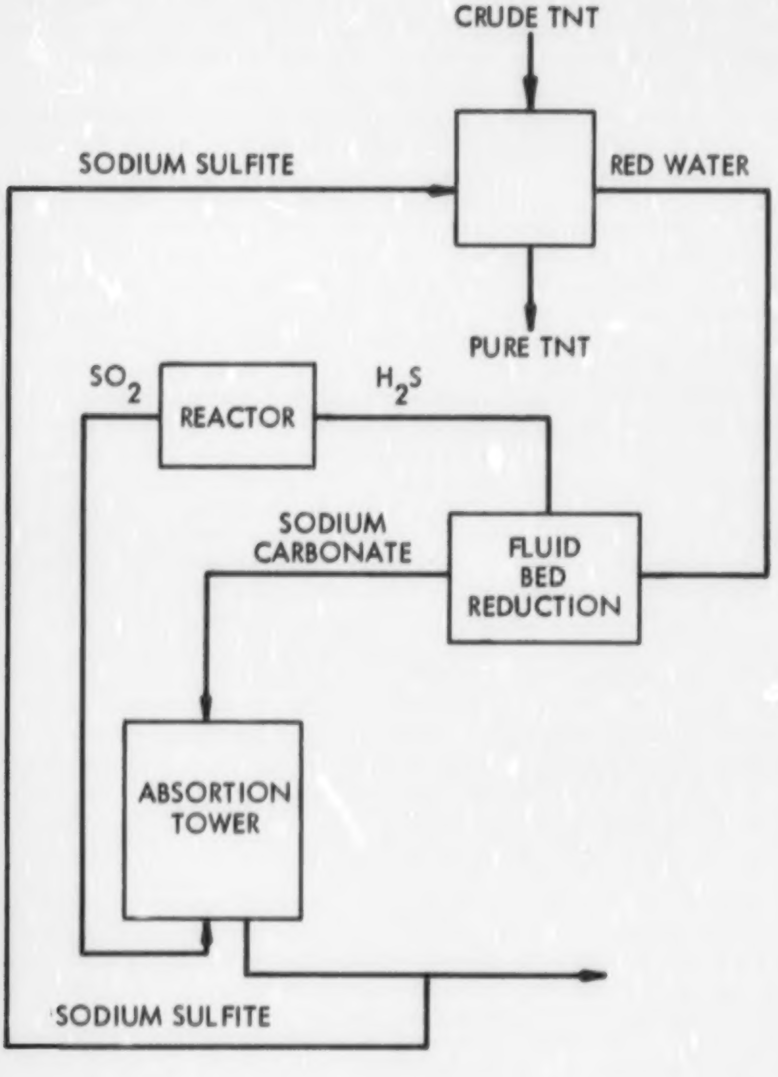

CRUDE TNT
SODIUM SULFITE
RED WATER
PURE TNT
SO_2
REACTOR
H_2S
SODIUM CARBONATE
FLUID BED REDUCTION
ABSORTION TOWER
SODIUM SULFITE

Figure 2 - Recycle of Red Water Wastes

d. Among other results, these researches found that more acidic waste pH increased the adsorption of α-TNT by the carbon. Thus at pH 1.4, "n" from the Freundlich isotherm plot was 1.6 while at pH 7.0, "n" was measured at 5.2. Generally the value of "n" is inversely proportional to the efficiency of a particular carbon. Further, the adsorption capacity of the carbon was somewhat enhanced with acidic raw wastes, although yielding less than half the measured capacity for pure α-TNT in distilled water of 0.675 lbs TNT/lb carbon. The greater capacity of 0.675 lbs/lb is frequently cited, however, in discussing the use of carbon to treat TNT wastes such as pink water, which theoretically is predominately α-TNT.

e. In short detention time (2.5-3.0 minutes) carbon column studies, for pure α-TNT in distilled water, efficient TNT removal occurred up to a total throughput of 2150 bed volumes. However, carbon column treatment of raw waste (red water) resulted in almost instantaneous breakthrough of both Silas-Mason reactable substances and color (16h). With longer detention time in the columns (15-25 minutes) improved TNT removal occurred, although color breakthrough was again very rapid. Carbon capacity for TNT at these detention times and pH 1.5 was 0.124-0.175 lbs/lb. Gas chromatography analyses of the carbon column effluent indicated complete removal of DNT and TNT, even after the Silas-Mason test showed breakthrough of Silas-Mason reactable substances. Thus, the carbon appears effective in removing DNT and TNT, but not effective in removing some of the other constituents of the red water, and its application for red water treatment appears doubtful. Further, the sum of TNT and DNT concentration measured in the raw waste by gas chromatography (GC) exceeded the concentration by the Silas-Mason procedure (52.6 vs 46.5 mg/l). Other substances detected by GC did not show up by the Silas-Mason technique (16h). These results raise serious questions concerning the specificity and sensitivity of the Silas-Mason procedure relative to monitoring red water quality. Chromatography methods such as gas, liquid-liquid, and thin layer, for detecting explosives in wastewater, many of which were developed at NSWC White Oak, appear more reliable and sensitive than the Silas-Mason procedure.

f. Edwards and Ingram (161), in exploring chemical treatment of TNT wastes, found that reducing chemicals such as sulfur dioxide and $Na_2S_4O_7$ were ineffective in reducing the color of red water. However, the use of chemical oxidants appears more promising. Schott, et al. (161) reported that chlorination at dosages of 5 to 20 mg/l reduced color in red water 25 percent or more, while bromination at equivalent dosage was twice as effective as chlorination. Ozonation as a method of treatment was disappointing, with up to 24 hours of ozonation yielding only 30 percent reduction in color. Recent success with UV-catalysis in ozonation of refractory organics (16m) suggests that ozonation treatment might benefit from the application of this technique and indeed, there is preliminary evidence to indicate that TNT wastewater can be successfully treated by UV-catalyzed ozonation (15z, 3z). UV ozonation generates a singlet oxygen, a reactive chemical species which is undoubtedly responsible for destruction of the nitrobodies. Other methods of generating singlet oxygen may become more economical than UV-ozone (15zq).

g. Although there has been no effort directed toward land disposal of red water, work is being done at NAD Crane on soil disposal and soil microorganism biodegradation of waste TNT (14j, 14t). The toxicity of TNT to some organisms is well documented, and its presence in soil may interfere with normal soil microbiological activity. Indeed, there is already evidence that the presence of TNT in soil impedes the degradation of paper, indicating that toxic side effects may preclude this method of disposal. Soils have been reported as effective in adsorbing TNT, up to 0.1 percent by weight (16q). If concentration on the soil proceeds more rapidly than degradation, localized TNT deposits could build up to hazardous levels in the soil.

8. Summary

a. The current practice of evaporative concentation of red water, with either sale to the paper industry or incineration and land disposal of ash, is unsatisfactory for several reasons. Concentration and incineration is costly in terms of energy requirements and, in fact, the proposal by Newport AAP to also concentrate and incinerate pink and yellow water along with red water is difficult to understand. Pink water and yellow water are extremely dilute solutions as compared to red water, and can be treated by processes described subsequently in this chapter.

b. Further, with the disappearance of the paper industry red water market, the need to incinerate all red water and dispose of the large quantities of resulting ash will increase the energy demand, as well as represent a potential hazard for ground water and surface water contamination by leaching of ash stockpiles. Avoidance of this problem would require containment and treatment of ash pile runoff, although certainly the simple lime treatment proposed for Newport AAP would not be adequate. Incineration is a terminal process, negating any possibility of by-product recovery. Both evaporation and incineration yield a pink water condensate which should receive further treatment, despite the current practice of discharge without treatment. In addition, there are severe air pollution consequences associated with incineration, including the emission of particulates plus oxides of nitrogen and sulfur.

c. The lack of success shown in studies of red water treatment by activated carbon, reverse osmosis, acidification and fluidized bed reduction leave only two viable alternate treatment technologies under investigation. These are the Tampella process and UV-catalyzed chemical oxidation. Neither has been proven at pilot scale. Major efforts should immediately be directed toward an intensive evaluation of each of these procedures while, as a back-up to their possible lack of success, preliminary studies should be undertaken to identify and assess other potential treatment methods.

d. Special attention should be given to the ineffectiveness of reverse osmosis treatment, failing both in the capability to achieve acceptable levels of concentration and to prevent leakage of pollutants across the membrane. This is a deficiency characteristic not only for explosives wastewaters, but for many other industrial wastes (16zy). The deficiency lies in the membranes available for reverse osmosis systems and, despite the early promise of reverse osmosis, its use remains severely restricted. A major research effort is warranted to develop more reliable and acceptable membranes.

9. Waste Sources

Pink water comes from both TNT manufacturing plants and LAP's. That from manufacturing plants arises from: nitration fume scrubber discharges; red water concentration distillates; finishing building hood scrubber and washdown effluents; and possibly spent acid recovery wastes (2b). An additional source of pink water is from demilitarization washout of munitions containing TNT. However, demilitarization is not a part of the scope of this study. The first two sources of pink water above may contain TNT isomers and dinitrotoluenes. Pink water from LAP's contains essentially α-TNT, frequently contaminated with RDX, HMX, wax or other additives. It has been reported that the effluent of the TNT spent acid recovery plant at Radford AAP contains a nitrobodies discharge of 35-371 lbs/day (4c, 8c). Table 1 summarizes the plants having pink water waste. Laundry waste waters have also been reported to contain TNT. Table 2 summarizes available data on the nitrobody content of pink waters from various sources. In general, evaporator condensate is relatively low in TNT, although Neal (3f) reported that this wastewater contains 150 mg/l TNT. LAP wastewater is higher in TNT, which may exceed 100 mg/l. If the data for scrubber water (Holston AAP and NAD McAlester) are representative, TNT content from this source is also high. Figure 3 shows the solubility of TNT in water as a function of temperature (13a). Despite the relatively low TNT concentration of evaporator condensate, the mass discharge may be substantial. For example, at full TNT production, the condensate discharge for Joliet AAP is projected at 325 gpm (8d). At a TNT concentration of 4 mg/l, this represents a daily discharge of 15.6 lbs TNT.

10. Current Treatment Practice

a. At present, only pink water from some LAP washdown and scrubber operations is treated. Processes in use include prefiltration plus activated carbon adsorption at Joliet and Iowa AAP's, and evaporative and leaching ponds at Cornhusker, Milan, Louisiana and Lone Star AAP's, and NAD McAlester. One unique disposal plan is to be employed at Newport AAP, where pink water will be sent to the red water evaporative system. Excess water will be vaporized and the concentrated solution treated along with concentrated red water, by incinerator (3f). In all cases, the pink water flows through sumps prior to treatment, to remove settleable solids. These sumps are mucked out at regular intervals, and the sludge taken to burning grounds for disposal.

b. Most Army and Navy plants actively developing pink water pollution abatement facilities propose to use activated carbon treatment, since this technique has been proven effective, whereas possible alternative technologies such as polymeric resins and biological treatment are still in the investigative stages.

Table 1. Plants With Pink Water Waste*

Army	Navy
Holston	Crane
Iowa	Hawthorne
Joliet	McAlester
Kansas	Yorktown
Lone Star	
Louisiana	
Milan	
Newport	
Radford	
Volunteer	

*See Volume I for detailed information on plant activities.

Table 2. Reported TNT Concentrations in Pink Wastewaters, mg/l

Plant	Evaporator Condensate	Clean Up LAP	Scrubber Water	Laundry Wastewater	Reference
Joliet AAP	1.4	178.3			1g(3)
	3.7-6.1				8d
	4.4				3v
				2.9	8e
	16				3f
NAD Crane					
Rockeye		40.1			14f
Plant A		5.8-11.2			14f
Plant B		20.2			14f
Holston AAP		3-9*	2-22		5d
Radford AAP	7.3				6d
		90-175			3w
		75			2b
NAD McAlester		30.6-38.4			14u
			30-80		15za
Iowa AAP		86.9			13a
				25.4	13c
Milan AAP		<1			2b
Louisiana AAP		80			2b
Cornhusker AAP (inactive)		57		2.7	2b

*From incorporation of TNT into Composition B.

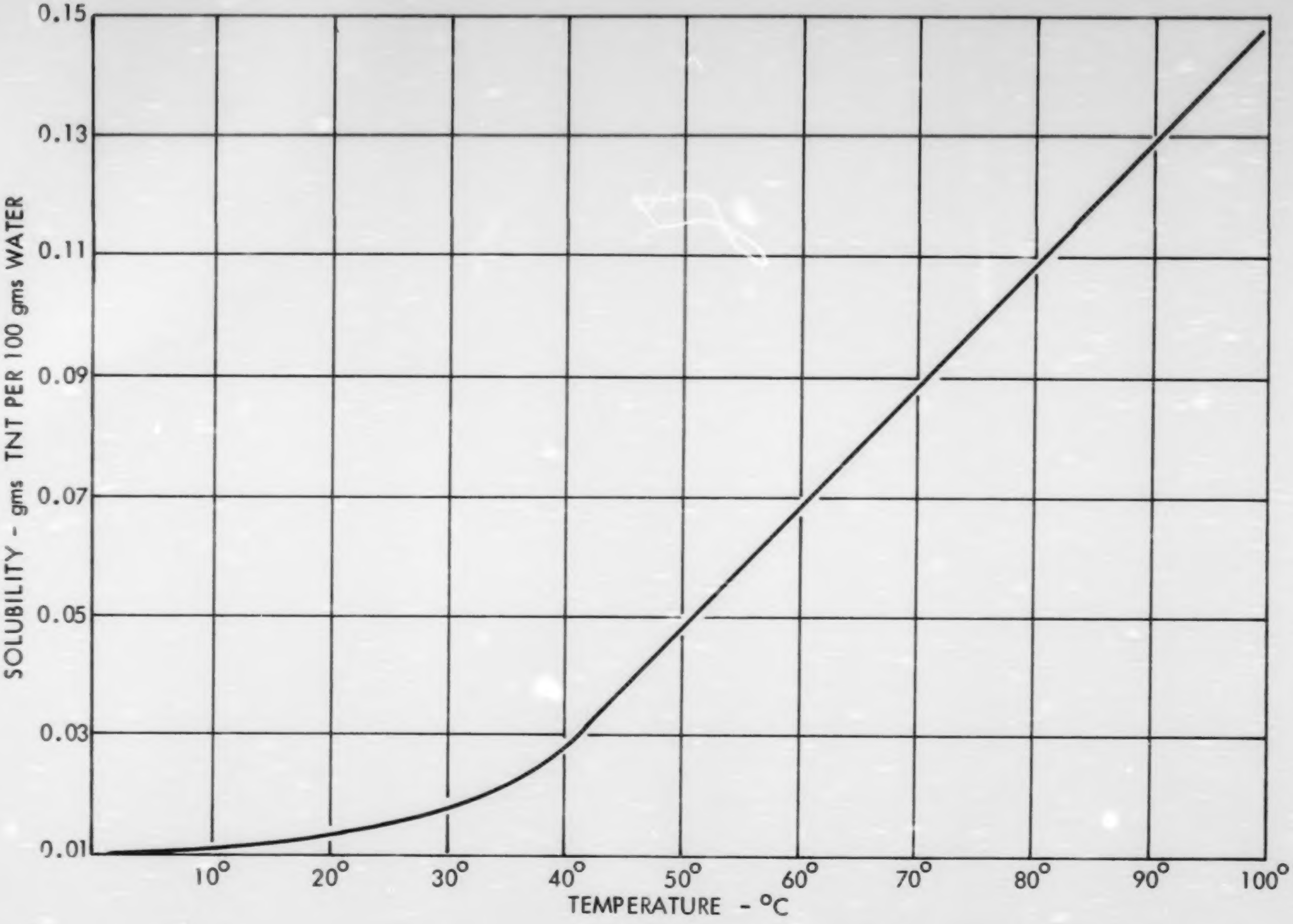


Figure 3 - Solubility of TNT in Water (13a)

c. Two carbon systems are currently in operation, one at Joliet and one at Iowa AAP. Joliet uses a two column series downflow system; and Iowa a two column expanded bed parallel upflow system. In both installations, the carbon beds are preceded by sumps to remove settleable solids, and diatomaceous earth filters to remove suspended solids carried over from the sumps. The basic layout is the same for both systems, as represented in Figure 4, a schematic of the Iowa installation (3i). Both installations are used to treat LAP wastewater. Because of the explosive material trapped in the diatomaceous earth filters, the filter material is used only until clogged, and then burned. Exhausted carbon is also destroyed by burning, since there is not yet an accepted way to regenerate it (15zb).

d. The successful use of carbon to treat TNT wastes was reported more than 20 years ago. Ruchhoft, et al. (16q) studied the treatment of both pure α-TNT (colorless) and TNT wastewaters in which color had developed. For the colorless solution, at a TNT concentration of 121.8 mg/1, they found up to 99.5 percent removal of TNT was possible with powdered carbon, and that powdered carbon was more effective than granular. Much less effective TNT removal (40.0-48.7%) was found for the colored TNT wastewater. The effect of color development on carbon treatability has been confirmed by Nay, et al. (16r). These authors concluded that as the waste color intensity increased, the waste became more toxic to microorganisms and more refractory to biodegradation, and treatment by any process, including carbon adsorption, became more difficult. While activated carbon was effective in removing both color and TNT, the development of color significantly decreased the carbon adsorptive capacity for TNT. Their results are presented in Figure 5 (16r). These workers also reported that among other factors which caused color intensification was adjustment of wastewater pH from an acidic to near-neutral value, with exposure to light enhancing color development. Spano, et al. (16s) reports that pink wastewaters are typically initially acidic (pH 3-4) and colorless.

e. Experience with carbon treatment of LAP pink water at Joliet AAP has been good. Wastewater passing through the system is subjected to two-step treatment. First, it is filtered in a diatomaceous earth filter to remove gross and suspended solids. Then, it is pumped downward through two carbon columns, to remove dissolved explosives contaminants (TNT and RDX). The columns are connected in series and are piped so that the columns may be used in either order. This allows the final effluent always to leave the column most recently charged with fresh carbon. Each column has dimensions of 9-foot height by 30-inch diameter. The carbon charge is 960 lbs. of Filtersorb II, changed monthly. The average wastewater volume treated by the system is 6165 gpd (1g(3)). Table 3 summarizes operating data for the system, presenting range and average results from eleven samples collected by AEHA personnel in 1972 during a two-week study of Joliet AAP (1g(3)).

f. The data of Table 3 indicate a raw wastewater of somewhat alkaline pH, high in solids and explosives. It is noteworthy that the

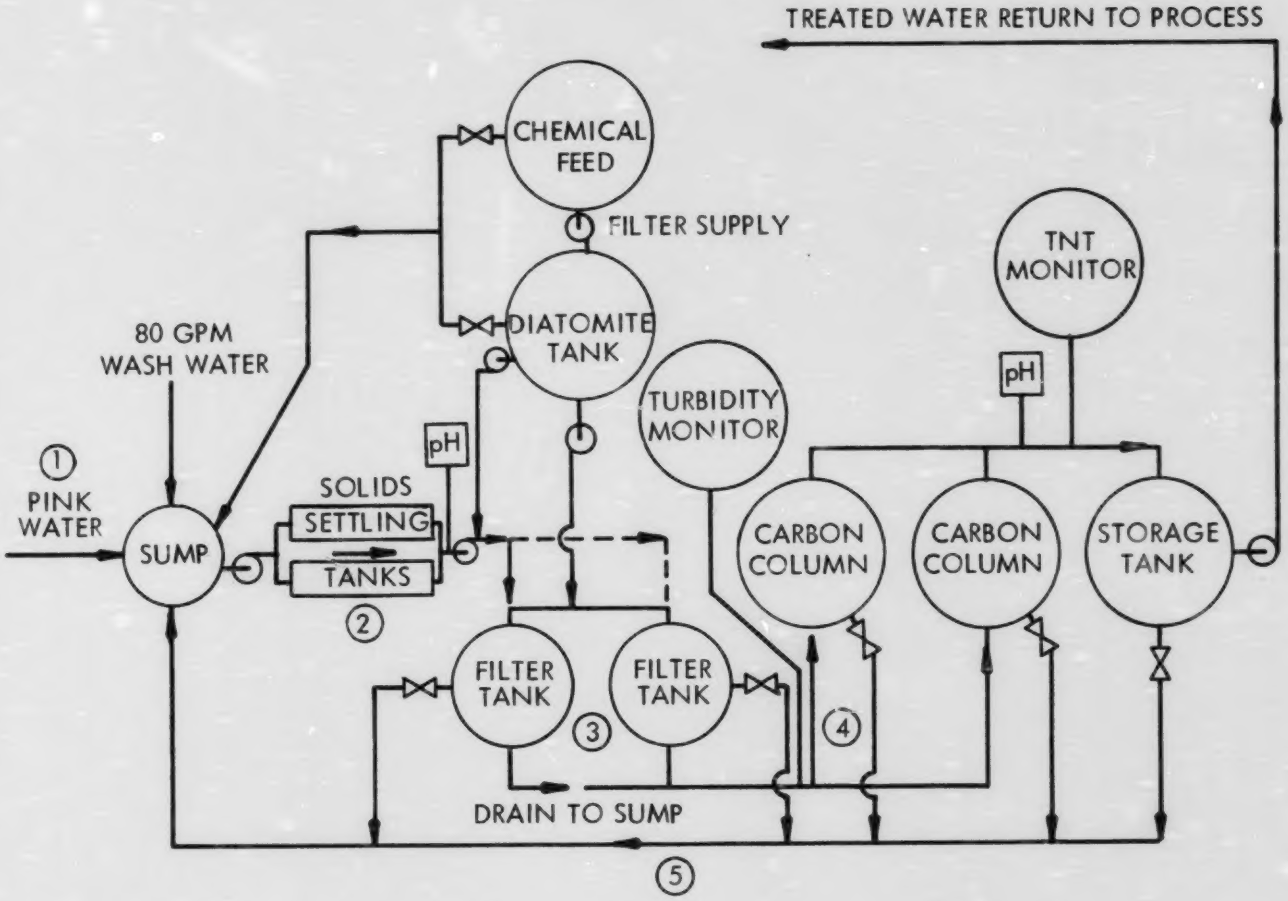

TREATED WATER RETURN TO PROCESS
CHEMICAL FEED
FILTER SUPPLY
TNT MONITOR
80 GPM WASH WATER
DIATOMITE TANK
pH
TURBIDITY MONITOR
①
PINK WATER
SUMP
SOLIDS SETTLING TANKS
pH
②
CARBON COLUMN
CARBON COLUMN
STORAGE TANK
FILTER TANK
FILTER TANK
③
④
DRAIN TO SUMP
⑤

Figure 4 - Pink Water Treatment for Loading, Assembling, and Packing Operations

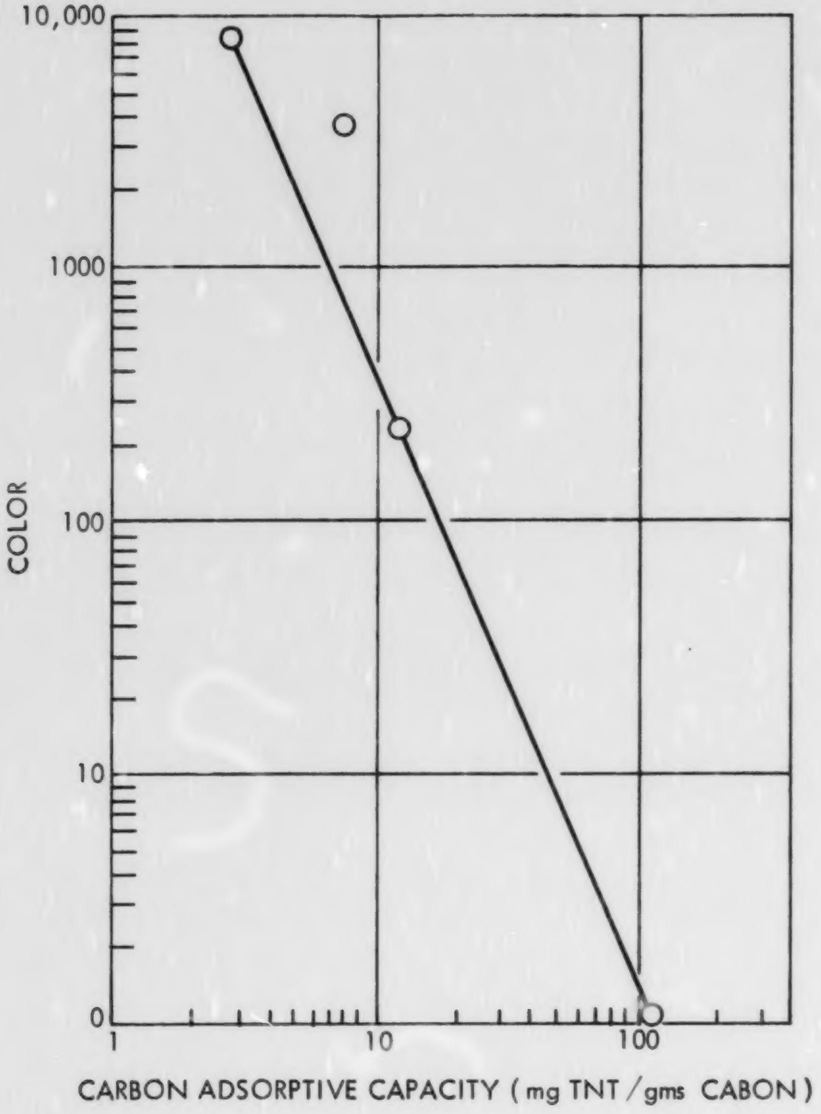


Figure 5 - Relationship of Color and Carbon Adsorptive Capacity for TNT

Table 3. Performance of LAP Wastewater Treatment System at Joliet AAP (1g(3))

Parameter*	LAP Influent		Effluent From:						Average Percent Change
			Diat. Earth Filter		1st Carbon Column		2nd Carbon Column		
	Range	Average	Range	Average	Range	Average	Range	Average	
pH	6.8-8.4	7.9	7.6-8.6	7.9	7.6-8.2	7.8	6.7-8.0	7.7	-
Total Solids	903-1790	1401.5	959-1796	1418.5	794-1791	1138.3	762-1497	1069.8	23.7
Suspended Solids	220-336	138.5	26.0-271.0	108.6	0.0-40.0	8.4	0.0-7.0	1.2	99.1
TOC	93-188.4	121.1	100.0-162.0	121.1	5.9-64.0	24.3	7.8-20.9	12.1	90.0
Kjeldahl-N	10.3-25.4	17.0	8.9-23.0	15.3	4.4-8.6	7.2	4.0-4.9	4.6	72.9
TNT	156.2-235.0	178.2	143.5-213.0	175.7	0.0-111.2	14.7	0.0-25.0	3.7	97.9
RDX	87.5-180.0	145.2	87.5-185.0	148.9	0.0-77.5	30.1	0.0-46.4	19.5	86.6
Color	-	-	-	-	5.0-20.0	10.0	0.0-20.0	8.0	-

*All units except pH and color in mg/l. Color in PTU.

diatomaceous filter accounts for only 21.5 percent removal of suspended solids, with the bulk of removal occurring in the first carbon column. The filter also accounted for no significant removal of explosives.

g. The AEHA*study team suggested that filter efficiency could be improved by implementing an effective maintenance schedule. They further suggested that if the wastewater were maintained slightly acidic, most of the TNT would remain as α-TNT, and thus be more readily removed by carbon adsorption. The final effluent is of general good quality, with suspended solids, TNT and RDX averages of 1.2, 3.7 and 19.5 mg/l, respectively. The range of data in Table 3 suggests that by close process control, effluent levels of less than 0.1 mg/l of TNT and RDX can be achieved. However, a recent claim by Rosenblatt, et al. (2b), that the Joliet system achieves an average effluent of less than 1 mg/l is not substantiated by the data of Table 3.

h. In studies to determine the comparative cost and efficiency of various carbons for the Iowa AAP treatment system, it was found that the carbon required per 1000 gallons wastewater treated ranged from 18.3-40.9 lbs. (13b). The loading criterion was grams of carbon needed to reduce TNT from 65 to less than 3 mg/l. The Iowa system employs parallel upflow columns, preceded by a diatomaceous earth filter. The columns are recharged with fresh carbon when the effluent TNT level reaches 5 mg/l (13c). Effluent TNT levels from 0.1 up to 180 mg/l have been reported, however (13c). The system treats about 25,000 gpd of pink water (2b).

i. Data available from Radford AAP for pilot carbon treatment of pink water over the period 6 September, 1973-28 February, 1974 and reported in Table 4. The effluent pH is even more basic than reported for Joliet in Table 3. Effluent total solids are comparable, suspended solids much higher, and TNT significantly lower at Radford. However, influent data were not available.

j. An extensive pilot study of a carbon system was recently carried out at NAD Hawthorne (15zc, 14zb). Several alternatives to the diatomaceous earth filter were investigated, due to its tendency to cake up when the wastewater contains wax. Alternatives studied were multimedia (sand and coal) pressure filters and air flotation. Both multimedia and diatomaceous earth filtration performed comparably. In one series of runs, influent TNT averaging 1018 mg/l was reduced by the combination of air flotation and sand filtration to 414 mg/l. The same waste stream was reduced to 411 mg/l TNT by air flotation plus diatomaceous earth filtration (14zb). Experiments with TNT removal from wastewaters of Composition A-3, Composition B, HBX-1 and Picratol showed equally comparable removal efficiencies for sand filtration versus diatomaceous earth filtration. Thus, selection of best filtration techniques can be made on the basis of cost-effectiveness and ease of operation. Cooling of the wastewater prior to filtration was also investigated. This pretreatment was intended to precipitate wax, TNT and other soluble components, which would be removed prior to the carbon, and thus extend the carbon life. Cooling was successful, although some difficulties were encountered with explosive precipitate coating the cooling system.

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* U.S. Army Environmental Hygiene Agency

Table 4. Carbon System Effluent at Radford AAP (6d)

Parameter	Range	Average
pH	7.7-9.3	-
Total Solids	552-1870	951.3
Suspended Solids	2.0-125	38.7
TNT	0.0-2.4	0.91

k. One of the most serious deficiencies of the carbon system is the lack of current capability to regenerate the exhausted carbon. As a result, the carbon is disposed by incineration after a single use. This lack of regenerative capability results in three disadvantages for carbon treatment: (1) the economics of carbon use are mugh higher than normal for other industrial wastewater carbon systems, (2) there is no potential to recover and reuse the α-TNT waste product captured by the carbon, and (3) the incineration of the carbon is a potential source of air pollution.

l. Two regenerative techniques have been studied, thermal and solvent extraction. Eliassen (16t) reported in 1944 that activated carbon would treat TNT wastewater, but if the carbon is regenerated in a closed cell it is liable to explode. Recent tests by Rosenblatt, et al. (3c) confirm this in lab tests. They report that as the degree of carbon saturation with TNT increases from x/m of 0.217 to 0.675 (the saturation value), an exothermic reaction occurred within the thermal regeneration furnace. At the higher degree of saturation, explosion occurred in both an air and nitrogen atmosphere. At the lower degree of saturation (x/m = 0.217), there was no detectable exothermic reaction, and up to 80 percent of the TNT in the spent carbon was removed safely in 30 minutes at a furnace temperature of 900°F. Although the carbon was not retested in this study to determine its regenerated capacity, other sources report that the regenerated carbon recovers only about 60 percent of its original capacity (15y). The off-gas from the regenerator furnace was reported to contain water, carbon dioxide, nitrogen oxides and methane. Successful applications of thermal regeneration to spent activated carbon would thus produce air pollutants. Additionally, the low degree of saturation acceptable for thermal regeneration indicates that the carbon would be used only to one-third capacity before regeneration. The Army proposes to undertake pilot plant thermal regeneration studies, to determine equipment design criterion for possible GOCO plant implementation (3i).

m. Acetone, methanol and toluene have been investigated as chemical solvents for carbon regeneration (3c, 15s, 13f). The potential advantages of the method are: (1) regeneration takes place within the fixed bed; (2) TNT contaminated solvent can be reused as regenerant or as raw material in TNT manufacture; and (3) the carbon may be more completely saturated with TNT than is possible for thermal regeneration (3c). Spano, et al. (16s) in lab column studies, found that only 22.3 percent of the TNT was removed by two bed volumes of acetone. These preliminary and limited results are in contrast to pilot results with acetone regeneration of carbon, described below (13f). Rosenblatt, et al. (3c) also in lab scale tests on TNT saturated carbon, used a toluene wash, followed by acetone. The toluene removed 67 percent of the TNT, while the sequential wash with acetone removed only trace amounts of TNT. After stripping with toluene, the carbon was reused to remove TNT. An amount of TNT equal to that recovered in the initial toluene wash was again removed by the carbon. A second toluene wash removed 92.4 percent of the TNT adsorbed during the second carbon use. Thus it appears likely that the sorptive capacity approaches some constant level on repeated use, followed by toluene regeneration of the carbon.

n. In separate pilot plant studies at Iowa AAP, Brinck (13f) investigated solvent stripping of TNT-laden carbon by use of acetone, methanol, and toluene. The pilot study, involving in-place regeneration of carbon columns, yielded 92 percent TNT removal by acetone, 34 percent by methanol and 28 percent by toluene. Although acetone effectively removed the TNT, the carbon did not recover capacity equivalent to the TNT removed. The carbon was reactivated only to the extent of 43 percent, 33 percent and 31 percent for acetone, methanol and toluene, respectively (13f). Although the results of Brinck (13f) and Rosenblatt, et al. (3c) are somewhat conflicting relative to the efficiency of TNT stripping by acetone, both studies indicate only partial recovery of adsorptive capacity upon regeneration with either toluene or acetone.

o. An economic feasibility study of the regeneration of carbon by chemical means is underway at Edgewood Arsenal (3i).

p. With the exception of a demonstration scale biological treatment system to be constructed at NAD McAlester, all current construction plans for pink water abatement call for the use of carbon systems. Both up-flow and down-flow systems are under consideration. The up-flow system is easier to pump, but results in a lower carbon loading with TNT. Unless one of the carbon regeneration techniques now under investigation proves technically and economically feasible, a down-flow system will be used since the carbon can be loaded to saturation before disposal (15y). A down-flow fixed bed system with two columns in series appears to be optimal, as compared with other down-flow multi-column systems (3c).

q. At Joliet AAP, where carbon systems are already in use for LAP pink water, the same system is proposed to handle red water evaporator plant condensate (1g(3), 15zb). The proposed system will include a diatomaceous earth filter and two down-flow columns in series. The characteristics of the condensate are sufficiently similar to that of LAP wastes (Table 5), that a carbon system should prove effective. In general, the condensate represents a more dilute waste than the LAP pink water, particularly with regard to suspended solids and TNT. Indeed, it is noteworthy that Joliet AAP proposes to install a treatment system for a waste more dilute in TNT (0.1-2.6 mg/l) than the design TNT effluent for other proposed carbon systems.

r. NAD Crane proposes a recycle approach to handle fume scrubber water from their Mine Fill A Line. The scrubber water will be recirculated, through a settling basin and filter. Since the water should quickly become saturated with TNT, subsequent captured TNT would remain in the particulate form, and be removed by sedimentation and filtration (15ze). The recirculation system should negate the need for carbon treatment, unless blowdown from the recycled scrubber water becomes necessary.

Table 5. Comparison of Red Water Incinerator Condensate and LAP Pink Water at Joliet AAP (1g(3))

Parameter*	Condensate		LAP Pink Water	
	Range	Average	Range	Average
Temperature ^{o}F	162-176	170.2	-	-
pH	8.1-9.2	8.9	6.8-8.4	7.9
Conductivity	190-440	326.2	1364.0-9000.0	4082.1
Acidity	0.0-8.0	1.6	0.0-32.0	17.6
Alkalinity	52.0-244.0	180.0	164.0-356.0	289.3
Color, PCU	5.0-6.0	5.8	-	-
Total Solids	201.0-317.0	250.0	903.0-1790.0	1401.5
Suspended Solids	1.0-16.0	11.7	22.0-336.0	138.5
Dissolved Solids	185.0-302.0	238.5	881.0-1482.0	1264.8
Total Volatile Solids	119.0-250.0	192.0	426.0-954.0	547.6
Total Organic Carbon	31.7-39.0	35.3	93.0-188.4	121.1
Kjeldahl-N	15.1-24.0	18.0	10.3-25.4	17.0
Nitrates	2.4-4.6	3.4	-	-
Sulfates	26.0-44.0	37.2	-	-
TNT	0.1-2.6	1.4	156.2-235.0	178.2
RDX	-	-	87.5-180.0	145.2

*All mg/l except pH, temperature, conductivity and color.

s. NAD Crane will, however, use carbon treatment for clean-up water from their LAP operations (15ze). Table 6 summarizes the waste characteristics of one of the flows to be treated (the Rockeye LAP area). A concept engineering study for control of this TNT waste at NAD Crane recommends the use of carbon at two loading sites, over other alternatives, in light of its proven capability (14f). The wastewater to be treated will contain approximately 95 mg/l TNT, with a flow of 90-95 gpm at each site. Each carbon system will include a flow equalization tank of 100,000 gallons capacity, two diatomaceous earth leaf filters operating in parallel, and three parallel down-flow carbon columns. Flow will be equally distributed between the three columns. The use of down-flow parallel columns is a departure from the system used successfully at Joliet AAP (series down-flow) and Iowa AAP (parallel up-flow). It likely represents a compromise between the two types of systems, which will yield a more highly saturated carbon than the Iowa system, but less effective removal than a series system such as Joliet's. However, if a high suspended solids removal occurs, such as is experienced at Joliet, the proposed columns may well clog before the carbon is exhausted. To counter this possibility, the NAD Crane systems will incorporate carbon column backwash capabilities. A feasibility study report submitted to the concept engineer, nevertheless recommended use of the Joliet type system (14f).

t. At Yorktown Naval Weapons Station, a two column series carbon system has recently been installed at their pilot LAP facility. The system includes a diatomaceous earth filter, and is sized for a 20 gpm flow. Additional 20 gpm carbon systems are under construction at four other LAP facilities at the station. However, these latter four systems will consist only of a filter plus a single up-flow carbon column. The use of a single column is a departure from practice at other Army and Navy installations, but possibly reflects the design TNT effluent criteria of 5 mg/l or less (14r). This is a considerably higher TNT effluent than is achieved with the Joliet or Iowa AAP dual carbon columns.

u. Evaporative disposal is also a treatment technique currently applied to pink water. The successful use of evaporative treatment is dependent upon soil and climatological conditions. NAD Hawthorne (Nevada) successfully uses sumps, followed by evaporative ponds, to dispose of pink water resulting from fume and dust control (15zc). After evaporation, the residue is burned.

v. NAD McAlester (Oklahoma) has four lagoons to receive wastewater from various areas of the facility. Although all are designed to overflow, the regional net annual evaporative loss of 10 inches/year has, to date, resulted in no overflow from the lagoons (15za). Plant personnel expectation is that, at present wastewater discharge volumes, there should be no overflow, with the possible exception of the November-December rainy season. Wastewater sources include fume and dust scrubber water and clean-up water. A recent report on the impact of modernization of NAD McAlester indicated that a carbon treatment system will be installed to handle the TNT waste flows from the "A" plant

Table 6. LAP Wastewater Character for NAD Crane Rockeye Facility (14f)

Parameter*	Average	Range
pH	7.7	7.3-8.2
Temperature °C	10.3	5.0-17.9
Suspended Solids	15.0	0.0-110.0
Dissolved Solids	140.0	119.0-755.0
COD	44.0	12.0-84.0
TNT	40.1	16.8-87.2
RDX	0.0	0.0
HMX	8.5	2.4-16.0
Oil and Grease	70.0	6.0-153.0
NH_3-N	1.5	0.3-3.1
NO_3-N	0.8	0.0-3.9
Kjeld-N	2.7	1.1-3.5
Phosphorus	0.3	0.0-1.2
Chloride	18.0	8.0-51.0
Calcium	33.0	22.0-45.0
Sodium	67.0	5.0-275.0

*All mg/l except pH and temperature.

(14m). Installation of a demonstration biological oxidation ditch is planned for the "B" plant, allowing cost comparisons.

w. Both Louisiana and Lone Stone AAP's have been reported to use evaporative/leaching ponds for TNT wastewater (2b). At Louisiana AAP the wastewater (138,000 gpd) containing approximately 80 mg/l TNT, is trucked to leaching ponds. At times of heavy rainfall the ponds overflow (2b). Lone Star AAP wastewater is reported to have a volume of 20,000 gpd with TNT content of approximately 50 mg/l. This is trucked to holding ponds, which are reported to overflow due to heavy rains (2b). The experience of these two plants emphasizes the need to properly balance seasonal net evaporative rate with pond capacity, in designing evaporative ponds for final disposal.

11. Modifications and Alternatives to Current Treatment

a. Several alternatives to carbon adsorption and evaporative disposal have been investigated for pink water. These include: solvent extraction; reverse osmosis; adsorption onto fly ash; resin adsorption; ozonolysis; and biological treatment. Ozonolysis was discussed in the preceding section on red water treatment.

b. Solvent extraction using toluene in a bench scale (300 ml/min.) two stage continuous countercurrent extraction system was investigated at Iowa AAP (13a). Treating wastewater containing 87 mg/l TNT, the process was found to remove and recover up to 97 percent of the TNT. Using a 27:1 water to solvent ratio, the unit achieved an effluent TNT level of less than 3 mg/l. However a full scale unit for the Iowa AAP was estimated to require a 12,000 gph treatment capacity, with operating costs of $1.15 (1964 basis) per 1,000 gallons of water treated.

c. Treatment by reverse osmosis has been studied at Volunteer AAP (3f). Although the process is effective in concentrating the pink water, excessive TNT leakage through the available membranes has resulted in abandonment of further study of this process (15y).

d. The successful use of fly ash to adsorb TNT has been reported (16u, 16v), and fly ash was used at one time to reduce TNT in a creek at Iowa AAP (13a). However, Meek (13d) has reported that fly ash has a very low adsorption capacity for TNT, at 1.08 gm TNT per lb fly ash (0.0024 gm/gm ash). When compared to the capacity of carbon for TNT (0.4-0.7 gm/gm) the quantity of fly ash required becomes disproportionate, and ultimate disposal remains a problem, as with carbon.

e. The use of polymeric ion exchange resins has been investigated for TNT removal from LAP waters (3h, 14zb). One resin has been shown to be an effective adsorbent, with easy chemical regeneration and a long life cycle. Figure 6 presents results from multiple regeneration experiments with this resin, using acetone (3h). The resin, which is a copolymer of styrene and divinyl benzene, is sold as Rohm and Haas Amberlite XAD-4 (16s). Comparison studies of XAD-4 (16s, 14zb, 3za)

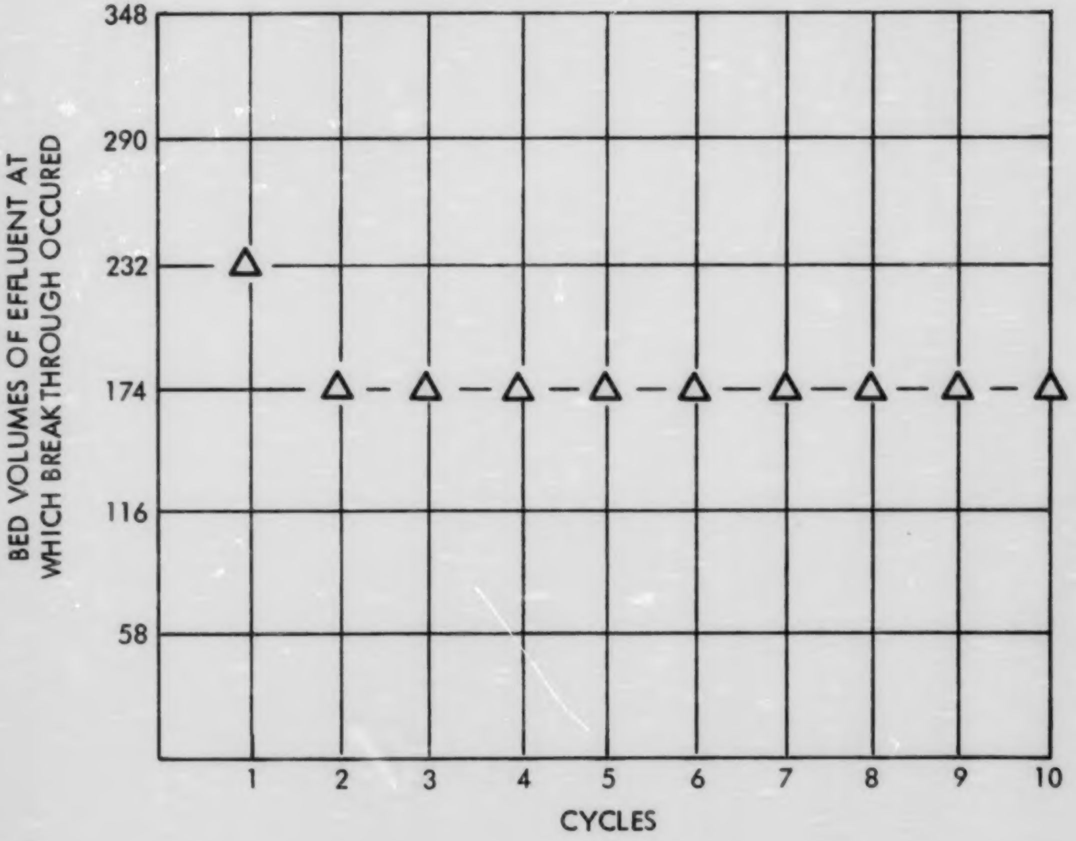

Figure 6 - Results from Multiple Regeneration Experiments

with activated carbon indicate that the two adsorbent materials have equivalent TNT capacity to the breakthrough point in a column. After breakthrough, carbon removal efficiency exceeds the resin. However, the possibility of multiple regeneration and reuse of the resin may offset this disadvantage. Another, and perhaps more significant disadvantage is that the resin column does allow some color components to pass through, while carbon is more effective in that respect. This suggests the possibility of a resin first stage followed by a carbon second stage series adsorption system.

f. In pilot studies at Iowa AAP, influent TNT of 81-116 mg/l was reduced to below 1 mg/l by resin adsorption. Saturation capacity of the resin is about 0.11-0.15 gm TNT/gm resin, with TNT breakthrough above 1 mg/l occurring at 40 percent of saturation capacity (16zzz). Acetone regeneration of the resin could be accomplished within two bed volumes of the resin column.

g. A disproportionate degree of effort is currently being directed toward evaluation of biological treatment processes for TNT wastes, considering the rather poor prognosis indicated by a review of historical records. For example, an early study by Schott, et al. (16i) indicated that neither activated sludge nor trickling filters could effectively degrade TNT wastes and that, in fact, treatment performance fell off rapidly with increased wastewater TNT concentration, indicating toxic effects upon the biological processes. Edwards and Ingram (16l) in another early study, likewise reported TNT wastes very resistant to biological attack. Results such as these led Rudolfs (16n) to conclude that TNT wastes cannot be oxidized biochemically, and purification cannot be expected in streams.

h. Despite such early evidence there is a great deal of literature (16w, 16z), and reports of on-going research, which indicate that TNT wastes are susceptible to biological treatment. Neal (3f) reports that because of the toxic nature of some of the organics in red water to microorganisms, it is necessary to dilute this waste with another waste for biological treatment. He further states that biological treatment, following neutralization, is possible. However, treatment for removal of color and dissolved inorganics should be by physical-chemical methods. Nay et al. (8e) confirms this requirement, at least for color removal, by other than biological treatment. In their studies, color removal by biological treatment with an activated sludge system was evaluated, but essentially no color removal was observed. Further, some of their data suggested that color development was closely related to bio-toxicity during treatment (16r). Table 7 reports the results of their activated sludge experiments. Unsatisfactory results with both activated sludge and trickling filters have also been reported in a recent treatment feasibility study for NAD Crane (14f). The concept engineering report resulting from these studies concluded that biodegradation of the TNT wastewater was not a technically feasible treatment method. In substantiation of the toxicity effect, it has been reported that nitrobody wastes from α-TNT manufacture are toxic to the environment when released into streams at concentrations of TNT greater than 2.5 mg/l

Table 7. Summary of Results: TNT Combination Wastes Treatability Runs - Color Removal (16r)

Run	TNT In (mg/1)	Color In	MLSS (mg/1)	Detention Time (hours)	TNT Out (mg/1)	Color Out (mg/1)	Color Removed (%)
1	5.0	103	1740	14	0.8	76	26
2	5.0	145	1500	7	1.4	61	58
3	5.0	131	1680	3	1.4	65	50
4*	10.0	101	1860	14	3.0	132	-31
5	10.0	121	2070	7	3.0	129	-13
6	10.0	120	1740	3	4.0	110	8
7	15.0	168	1910	14	4.2	240	-43
8	15.0	167	2070	7	5.1	264	-58
9	15.0	194	2050	3	5.5	272	-40
10	20.0	271	1680	14	6.6	210	23
11	20.0	274	1600	7	10.0	270	1
12	20.0	278	1750	3	10.0	225	19
13	25.0	284	1650	14	6.7	172	39
14	25.0	316	1580	7	10.3	319	-1
15	25.0	280	1600	3	10.3	264	5

ave. 3%

*R-4 was repeated 12 times to investigate MLSS saturation by TNT. Color removal during these 12 additional runs averaged 18% with a range of -5% to 30%.

(3h). Unless acclimation occurs in a biological treatment process, this would indicate a need for great dilution of the wastewater, prior to treatment. The successful application of biological treatment would also require that toxic by-products not be formed in the biodegradation of the waste.

i. Despite these factors, there is recent evidence that α-TNT, at least, is biodegradable and that, perhaps, other nitrobodies of the wastewater may also be susceptible to biological treatment. Claims of successful biodegradation of pure α-TNT, with addition of supplemental organic nutrients, have recently been made (14z). In none of those reports is there evidence of successful degradation of α-TNT without supplemental nutrients, and in no case has color been allowed to develop in the TNT solution prior to the degradation experiments. For example, Southgate (16w) reports successful treatment of TNT at concentrations up to 40 mg/l in domestic sewage, with trickling filtration. A 1970 Army study with bench scale activated sludge revealed that TNT could be reduced from 29 mg/l to 8-15 mg/l, when mixed with a glucose/peptone substrate of COD 802 mg/l (1s). This is typical of more recent results, which indicate that very high supplemental organic nutrient resources are required in order to achieve TNT biodegradation (14k, 16o, 16p). Nay, et al. (16p, 16r) have reported that the development of color makes the waste more resistant to biological treatment. The U. S. Navy is currently conducting a pilot scale study of an Oxidation Ditch at NOL White Oak (1a(3)), and is planning on installing a facility using this process for the treatment of pink water at NAD McAlester. In the current NOL White Oak study, cornsteep liquor is used as the supplemental nutrient. Although there is strong evidence that α-TNT, at least, is biodegradable, many factors indicate that biological treatment is not desirable. These factors include: the recognized toxicity of even 1-2 mg/l of TNT; the lack of definition of degradation by-products and their possible toxicity; the high supplemental nutrient demands for successful biological treatment; and the increased resistance of pink water, after color development, to biodegradation.

12. Impact of Air Pollution Control

Many Army and Navy facilities propose to install water scrubber systems as part of their air pollution abatement programs. When installed in TNT handling or LAP buildings, these scrubbers will generate additional pink water flows. Their TNT content should be similar to values shown in Table 2, and their treatability comparable to present pink water wastes.

13. Summary

a. Although the wastewaters of LAP activities are well characterized, pink water originating from other sources such as red water evaporative condensate, spent acid recovery, nitrator fume scrubbers, and laundry wastewater are not adequately characterized. Wastewater characterization data for these "secondary" pink water sources are required.

b. Although activated carbon treatment is being used successfully, and its use will be expanded at both Army and Navy plants, design and performance criteria are not well established. For example, there is preliminary evidence that low pH, and avoidance of development of color, will enhance treatment efficiency. Further study is required to assess the effect of such factors on carbon performance. A variety of upflow and downflow, series and parallel, single and multiple carbon column systems are in use or under construction. Design criteria for carbon (or any treatment) system must reflect uniform performance goals and effluent requirements. These have not been established. Uniform design criteria should be defined, reflecting such factors as: whether the carbon will be used once and disposed, or regenerated; required effluent color and TNT levels; effects of pretreatment, such as filtration, on carbon performance; and similar factors. The use of single columns, such as proposed at NAD Crane and NWS Yorktown, is questionable, in light of the present lack of definition of design criteria.

c. The current practice of use of carbon to saturation, with disposal by incineration, has several deficiencies including: preclusion of recovery of TNT; high cost for replacement carbon; and air pollution from carbon incineration. In light of the proposed widespread use of carbon systems, an intensive study of carbon regeneration is warranted. The potential for regeneration, particularly with solvents, is significant, and can overcome the disadvantages of the present system. Since final carbon system design must reflect whether or not the carbon can be regenerated and reused, systems now in the design stage should incorporate the flexibility for regeneration. Experience with acetone regeneration yielded high percentage recovery of TNT from spent carbon, but only partial reactivation of the carbon. This, however, may have resulted from saturation of the carbon active sites with acetone, which could in fact be readily removed.

d. Polymeric resin adsorption has potential as an alternate to, or in combination with carbon. Its major disadvantage is low TNT capacity, compared to activated carbon. However, it is capable of being regenerated, and of sustaining through multiple regeneration a constant level of performance. If satisfactory carbon regeneration techniques cannot be developed, a resin system, or a resin first stage with carbon second stage appear to be viable alternatives. For the second alternative, the second stage carbon would still require incineration, although there would be much less carbon required, as the second stage would act only as a polishing unit.

e. The present use of evaporative ponds is an economical method of pink water disposal. However, unless such ponds are sealed, significant wastewater loss may occur by leaching. A better understanding is required of the effects of such leaching on both soil and ground water quality. Further, the experiences of both Louisiana and Lone Star AAP's with pond overflow during rainstorms emphasizes the need to balance seasonal, rather than annual net evaporative loss with pond capacity.

f. Biological treatment of pink water, while superficially attractive, raises several serious questions. TNT is both bio-refractory and toxic. Such wastes are not typically susceptible to standard biological treatment methods. Experience to date suggests that TNT can be reduced in concentration in wastewaters treated biologically, providing large quantities of supplemental nutrient are added. An important question which must be answered is what biotransformations occur, and what is the nature and impact of these by-products in the receiving water? Further, biological treatment will apparently not reduce color and it is conceivable that tertiary treatment such as ozonation, ion exchange or activated carbon would be required for effluent from a biological waste treatment system.

SECTION III - ACIDS

14. Introduction

The three major acids associated with military explosives and propellants manufacture are acetic, nitric and sulfuric. Acids are not involved in LAP operations. Concentrated nitric and sulfuric acid mixtures are used in explosives intermediate nitration processes, as for TNT, nitrocellulose and nitroglycerin. Acetic acid is used in the preparation of acetic anhydride, and the manufacture of HMX and RDX. Treatment technology for both acetic acid and acetic anhydride wastewaters will be discussed in this section. Acetic acid is recovered and purified for reuse, but not manufactured by military explosives plants. Weak nitric acid is manufactured by the ammonia oxidation process (AOP), and processed to yield concentrated nitric acid. Weak sulfuric acid is manufactured or purchased, concentrated and fortified to produce oleum. Spent sulfuric acid is regenerated and reused at most manufacturing plants.

SECTION III-A - ACETIC ACID AND ACETIC ANHYDRIDE

15. Introduction

These products are manufactured only at Holston AAP. Acetic acid and acetic anhydride, together with nitric acid and ammonium nitrate, are used in the nitration of hexamine to produce a slurry of crude RDX or HMX. The slurry is vacuum filtered, and washed to remove residual acidity (Figure 7). Initial filtrates contain 10% acetic acid, 2-3% nitric acid and some RDX or HMX. This filtrate is distilled to recover weak acetic acid. Acetic acid is separated by distillation to 20% residual filtrate volume, and soluble explosive is recovered from the still liquor by crystallization at 30°C. The liquor is then treated with sodium hydroxide to convert residual ammonium nitrate to sodium nitrate and ammonia (which is recovered by vaporization and condensation). Acetic acid is neutralized to sodium acetate. The neutralized solution is currently stored in holding ponds at Holston AAP, but will be processed into fertilizer when a processing facility is completed (2c). Recovered weak acetic acid is concentrated to glacial (99%) acetic acid by azeotropic distillation. A portion is reused directly in HMX and RDX manufacture, while the remainder is used in the manufacture of acetic anhydride. This latter product is produced by cracking the glacial acetic acid in furnaces, with the water of reaction removed by condensation. Uncracked acetic acid from the reaction is removed by azeotropic distillation and recycled to the cracking furnaces. Keten gas, formed in cracking, is reacted with additional acetic acid to yield crude acetic anhydride. The crude product is refined by distillation, and used in HMX and RDX manufacture.

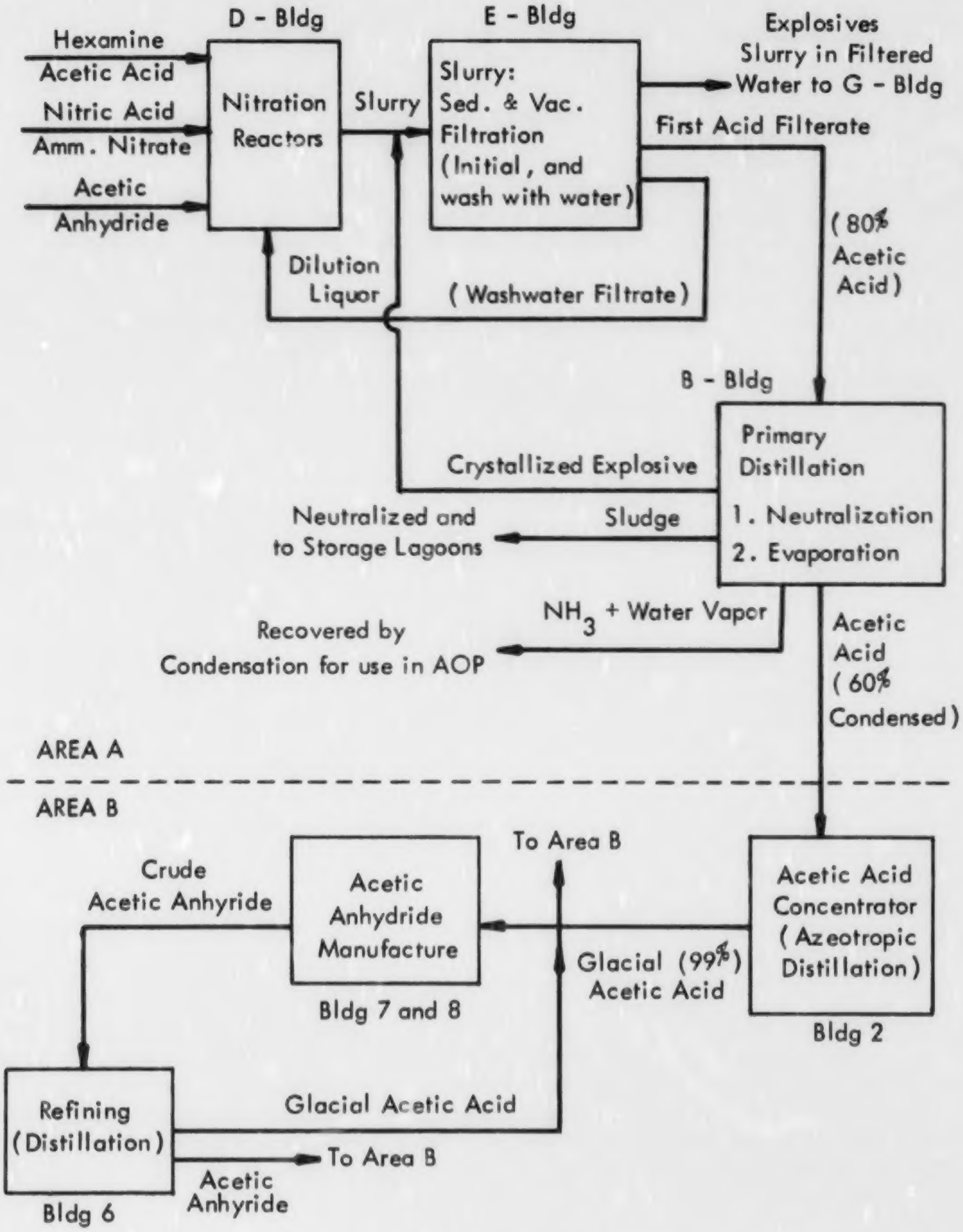
D - Bldg
E - Bldg
Hexamine
Acetic Acid
Nitric Acid
Amm. Nitrate
Acetic
Anhydride
Nitration
Reactors
Slurry
Slurry:
Sed. & Vac.
Filtration
(Initial, and
wash with water)
Explosives
Slurry in Filtered
Water to G - Bldg
First Acid Filterate
(80%
Acetic
Acid)
Dilution
Liquor
(Washwater Filtrate)
B - Bldg
Primary
Distillation
1. Neutralization
2. Evaporation
Crystallized Explosive
Neutralized and
to Storage Lagoons
Sludge
NH3 + Water Vapor
Recovered by
Condensation for use in AOP
Acetic
Acid
(60%
Condensed)
AREA A
AREA B
Crude
Acetic Anhydride
Acetic
Anhydride
Manufacture
Bldg 7 and 8
To Area B
Glacial (99%)
Acetic Acid
Acetic Acid
Concentrator
(Azeotropic
Distillation)
Bldg 2
Refining
(Distillation)
Bldg 6
Glacial Acetic Acid
To Area B
Acetic
Anhydride

Figure 7 - Acetic Acid and Acetic Anhydride Manufacture

16. Waste Sources

a. As shown in Figure 7, spent acetic plus nitric acid is recovered in the first filtration step of RDX or HMX, and sent to primary distillation. A wash with water, to remove residual acidity, is recovered and used as dilution liquor in the hexamine nitration procedure.

b. The primary distillation units receive contaminated weak acetic acid, and separate it into dilute acetic acid, ammonia and sludge fractions. Wastewater from the units averages 11.2 MGD* and consists primarily of cooling water mixed with some steam condensate containing acetic acid and ammonia, and equipment and building washdown water (1d(2)). This combined flow is reported to contain a COD of 20-56 mg/l (ave. 32), and ammonia-nitrogen of 0.7-5.6 mg/l (1d(2)). However, another source has reported an ammonia-nitrogen concentration of 900 mg/l in the contaminated fraction of the waste flow, with dilution by cooling water reducing this to 5 mg/l (3f). This same source reports that the waste also contains BOD, acetic acid and explosive, although concentrations are not given. Based upon individual discharge volumes (1d(2)), it is estimated that only approximately one percent of the total flow is contaminated process water, with the remaining 99 percent being cooling water.

c. The acetic acid azeotropic distillation facility concentrates dilute acetic acid received from the primary distillation line (Figure 7). The azeotroping agent added is n-propyl acetate. Water and n-propyl acetate are removed by evaporation, recondensed, and phase separated. The water from the phase separation decanter (sweet water) is passed through a flash column to recover as much n-propyl acetate as possible, before discharge to waste. The 99+ percent glacial acetic acid is removed from the column bottoms, for explosives manufacture reuse or for acetic anhydride manufacture.

d. During azerotropic distillation, there is an undesirable buildup of solids in the distillation column. Sludge bleedoff is necessary, with this material being sent to a sludge heating operation to distill additional acetic acid. The sludge is then discharged. Spent sludge may contain high concentration of heavy metals (Cr, Cu, Fe, and Mn) from corrosive destruction of distillation columns (1d(2), 4a). In addition to the flash column and sludge heater discharge (312,000 gpd), cooling and condenser water are discharged at 24 MGD (4a). Process effluents range in pH from 2.8 to 3.8 and contain nitromethane, methyl nitrate, acetic acid, n-propyl acetate, nitric acid and trace amounts of explosives (4a). Although the wastes are not well characterized, as a result of the high percentage of dilution water, available data strongly suggest that the process effluents are extremely high in COD, complex organics and possibly heavy metals.

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*million gallons/day

e. In the acetic anhydride manufacturing process, glacial acetic acid is vaporized and fed to a cracking furnace together with triethyl phosphate, a reaction catalyst. The vapor stream, containing ketene, is sequentially scrubbed by four recycling glacial acetic acid scrubbers to yield crude acetic anhydride. Vapor leaving the fourth scrubber goes through a once-through water scrubber, which discharges to waste. The vapor from the water scrubber goes to a barometric condensor. Non-condensibles vent to the atmosphere, and condensate is discharged as wastewater. The process effluent is reported as 0.5-0.55 MGD (4a), which is combined with a cooling water discharge of approximately 2.3 MGD (1d(2)). The process effluent contains acetic anhydride, acetic acid, acetaldehyde, acetonitrile, methyl nitrate, ethanol, methanol, ethyl acetate, propanol, propyl acetate and other organics. The water scrubber effluent BOD is reported as 743 mg/l (4a).

f. The final step in acetic acid recovery and acetic anhydride manufacture is refining of the crude acetic anhydride (Figure 7). Refining is by distillation in two-stage columns heated in the lower stage. Refined anhydride is withdrawn from the lower stage, sent to a second small column for removal of color bodies, and stored for use in explosives manufacture. The vapors from the top of the two-stage anhydride column contain acetic acid and acetic anhydride, plus some impurities. This vapor is condensed and sent to a stripping column where it is separated into acetic acid, anhydride bottoms (returned to the refining column), and acetic acid vapors. These vapors are concentrated to glacial strength by azeotropic distillation.

g. Sludges from the refining column are heated under vacuum to recover additional acetic anhydride. The residual sludge is discharged as waste (70,000 gpd). Sludge from the azeotropic stills is acidified with sulfuric acid to break down acetamide, heated to recover acetic acid, and discharged (8,100 gpd). There is also a 280 gpd flow from a flash column involved in acetic acid concentration. This flow is reported to contain acetone, ethyl acetate, and acetonitrile (methyl cyanide)(4a). These discharges are combined with cooling and condensing water, to yield a total discharge of about 9.5 MGD.

h. Table 8 summarizes available information on process and total waste discharge volumes, and Table 9 available information on combined discharge waste characteristics. Dilution water exceeds 98 percent of total discharge for all except acetic anhydride manufacture, for which it represents about 80 percent. Despite the high degree of dilution, kjeldahl nitrogen is notably high in the acetic anhydride refining effluent, as are phosphorus and sulfate. High COD's are indicated in the primary distillation effluent, and in Outfall 1 (Table 9) discharge from acetic acid concentration. Acetic acid is present in all wastewater where monitored, at less than 3 mg/l.

17. Effects of Water Management

The data of Table 8 indicate that strict segregation of cooling water from process waste will result in a ten to fifty-fold reduction

Table 8. Wastewater Volumes from Acetic Acid Recovery and Acetic Anhydride Manufacture

Process	Process Effluent		Cooling Water, MGD	Total Flow, MGD	Percent Cooling Water
	Source	Volume, gpd			
1. Primary Distillation	Steam Condensate	120,000*	11.1	11.2	99.1
2. Acetic Acid Concentration	Sludge & Flash Column	312,000	23.7	24.0	98.7
3. Acetic Anhydride Manufacture	Scrubber & Condensate	500,000-550,000	2.3	2.8-2.85	80.7-82.1
4. Acetic Anhydride Refining	Sludge & Condensate	78,380	9.4	9.5	98.9
TOTAL, MGD		1.01-1.06	46.5	47.5	97.9%

*Estimated.

Table 9. Combined Wastewater Characteristics from Acetic Acid Recovery and Acetic Anhydride Manufacture (1d(z))

Parameter*	Primary Distillation	Acetic Acid Concentration		Acetic Anhydride Manufacture		Acetic Anhydride Refining
		Outfall 1	Outfall 2	Outfall 1	Outfall 2	
Temperature °F	68.9	82.1	61.5	70.8	70.5	76.3
pH	7.7	7.3	7.8	7.7	7.3	7.8
$NO_2 + NO_3$-N	1.24	1.60	1.29	1.2	0.93	1.04
NH_3-N	1.72	-	-	-	-	-
Kjeld-N	1.73	0.8	0.5	0.12	<0.5	10.5
Sol. Phosphorus	< 0.03	0.72	0.04	0.04	0.06	34.6
Total Solids	319	132	137	122	126	319
Susp. Solids	11.7	7.6	5.4	6.0	9.1	6.7
Diss. Solids	307	124	131	116	117	121
COD	32	103	16	11	10	17.1
TOC	10	35.0	6.4	6.5	5.8	10.5
BOD	-	>67	1.0	2.0	<1.0	11.3
Sulfate	-	16.0	15.3	17.5	16.8	31.2
Phenol	-	< 0.05	<0.05	0.05	<0.05	<0.05
Acetic Acid	-	< 2.0	2.9	2.0	<2.0	1.8

*All as mg/l except temperature and pH.

in contaminated wastewater volume, yielding 1.0-2.4 MGD wastewater. It has been suggested that increased recycling, reuse, and recovery of process flows, together with cooling water segregation, could hold the total process wastewaters in the last three processes of acetic acid recovery and anhydride manufacture to 1 MGD or less (4a). Available data indicate that these process effluents would be extremely high in BOD and complex organics (including acetic acid), and perhaps toxic due to both toxic organics and heavy metals (from anhydride sludges). Segregation of process from cooling waters has been scheduled for the acetic acid concentration process, with process effluent neutralization and treatment in an aerated lagoon (1d(4)). Segregation of cooling and process wastes for all facilities is reported due by early 1976 (1d(4)). However, current expectation is that while implementation of waste segregation will proceed at Holston AAP on schedule, no actual treatment will be implemented until operation of the lagoon commences in February, 1976 (4a).

18. Current Treatment Practice

Pollution from acetic acid use results from the acid recovery and acetic anhydride manufacture processes. All spent acid is recovered, with dilute acid wash waters recycled as dilution liquor to RDX and HMX nitration processes. Sludge from primary distillation of acetic acid filtrate is neutralized with sodium hydroxide and held in storage lagoons. When a sludge processing plant is completed, this sludge will be converted to fertilizer, and sold. Wastewater from primary distillation, at 11.2 MGD (99.1% cooling water), is discharged without treatment. All wastewaters and sludges from acetic acid concentration and acetic anhydride manufacture and refining are currently discharged without treatment.

19. Modifications and Alternatives to Current Practice

a. By flow segregation, process wastewaters can be reduced to 120,000 gpd in Area B (primary distillation) and approximately 1 MGD in Area A (acetic acid concentration, and anhydride manufacture and refining). In addition it appears likely that in Area A best treatment will dictate separate collection and handling of the sludge and liquid fractions of the process effluents. Separate sludge handling has already been implemented for the primary distillation process in Area B.

b. Current plans for the liquid waste from primary distillation are to combine it with other liquid wastes from explosives manufacture and treat in an aerated lagoon (3f). However, bench scale attempts to biologically treat and carbon adsorb the wastes have been unsuccessful (5c). Biological treatment by activated sludge and trickling filtration resulted in effluent COD concentrations of 55 and 87 mg/l respectively, for influent COD values of about 350 and 450 mg/l. Difficulties with sludge bulking were also experienced in the activated sludge treatment. Denitrification experiments were successful in nitrate removal, although buffering of the system was required to maintain a pH below 9. Carbon adsorption experiments on both raw waste and biologically treated effluent yielded unfavorable adsorption isotherms, and a carbon column effluent of 16 mg/l BOD, for the biological process effluent, with influent of about 40 mg/l (5c). These preliminary carbon experiments also indicated rapid breakthrough.

c. The biological treatability results cited above suggest that treatment of the primary distillation wastewater by the proposed aerated lagoon may be unsuccessful. Due to the relatively small quantity of wastewater from primary distillation, serious consideration should be given to separate treatment of this flow. Among processes which should be considered are chemical coagulation and ozonation, perhaps followed by carbon adsorption or biological treatment.

d. Initial plans for wastewater treatment in Area A called for segregation of cooling water from process effluent, to be treated by neutralization and an aerated lagoon which was to incorporate biodenitrification (3h, 1d(4)). However, serious questions have been raised concerning the suitability of aerated lagoon treatment (4a). These questions relate to the level of treatment achievable by the aerated lagoon, the reliability of the process, and the fact that bioassay studies on Area A wastes indicate a high degree of toxicity (4a). The presence of toxic materials would seriously interfere with the efficiency of the proposed biological treatment. Since the wastes are not well characterized, it is not known which process effluent or effluents contribute to the toxicity effects. If biological treatment is to be implemented, however, toxic waste streams must be segregated for pretreatment to reduce toxixity, or alternately totally separate treatment by physical-chemical means.

e. A recent architect/engineer treatment concept report to Holston AAP suggests a sequence of activated sludge, followed by denitrification, mixed media filtration, and tertiary treatment if required to remove toxic substances. The tertiary treatment process has not been selected (5b). An activated sludge-denitrification system is to be pilot tested at Holston AAP (15zi). Providing toxic components do not interfere, this system should achieve acceptable treatment for BOD, nitrogen and suspended solids. It will not achieve satisfactory phosphate removal, phosphate being particularly high in the anhydride refining effluent (Table 9), as is sulfate and kjeldahl-nitrogen. Although the wastes of Area A are not well characterized due to the high percentage of dilution (cooling) water, such process stream constituents indicate that a more reasonable and effective approach to selection of treatment process would involve improved characterization of each process effluent, and consideration of individual treatment, such as phosphate precipitation, carbon adsorption, and chemical oxidation of those process effluents which show unusual composition.

f. Sludges resulting from acetic acid concentration and anhydride manufacture and refining should be separately handled and disposed. Recent information is that serious consideration is now being given to incineration of these sludges in a coal gasification plant at Holston AAP (15zi). Should this not prove feasible, the most probable alternative is to dewater and remove these sludges to approved landfill.

20. Impact of Air Pollution Control

Several side reaction products result from the manufacture of HMX and RDX, and are returned with the used acetic acid to the acetic acid recovery and purification process. These side products include methyl nitrate, methyl acetate, propyl formate and propyl acetate. At present, these contaminants are released as air pollutants in the vent gas from the acetic acid azeotropic distillation system. Because of the toxic and sensitive nature of methyl nitrate, these materials will ultimately be contained within the system by condensation, and handled as liquid wastes (3h). Preliminary biodegradation studies by the Army on decanter "sweet water" from the acetic acid recovery process indicate better than 97% methyl nitrate reduction, with other contaminants reduced by at least 90% (3i). Results are reported in Table 10. Based upon these biological treatability studies, high effluent levels of organic constituents are to be expected, and a tertiary process such as carbon adsorption will likely be required.

21. Summary

Despite the lack of reliable waste characterization data, which results from the high degree of process effluent dilution by cooling water, and indications that at least some process effluents are toxic, current plans call for biological treatment of acetic acid and anhydride wastes. Serious questions have been raised concerning the suitability of biological treatment, which will in any case be ineffective for phosphate control for the anhydride refining effluent. Final plans for waste treatment should be preceded by waste characterization studies, and both biological plus physical-chemical pilot treatability studies on individual as well as combined process effluents.

Table 10. Biodegradability of Acetic Acid Recovery Decanter Sweetwater (31)

Component	Concentration, mg/l		Percent Reduction
	Initial	Final	
Methyl Nitrate	616	19	96.9
Methyl Formate	12	-	-
Acetone	18	-	-
Methyl Acetate	1,266	25	98.0
Ethyl Acetate	49	-	-
Propyl Formate	12,548	502	96.0
Nitromethane	1,232	16	98.7
Propanol	4,451	13	99.7
Propyl Acetate	"High"	999	-

SECTION III-B - NITRIC ACID-MANUFACTURE AND CONCENTRATION

22. Introduction

a. Facilities to manufacture weak nitric acid, by the ammonia oxidation process (AOP), are available at Badger, Holston, Indiana, Joliet, Newport, Radford, Sunflower and Volunteer AAP's. All except Holston AAP also have facilities to produce concentrated nitric acid by the sulfuric acid dehydration technique. Holston AAP uses a hot magnesium nitrate dehydration process for nitric acid concentration (3f). Similar processes are used to produce weak and concentrated nitric acid in the commercial explosives industry, and that industry's waste characteristics and pollution abatement technology have been described in a recent report (4d).

b. Weak nitric acid is used to produce concentrated nitric acid, for nitration of explosives intermediates. Spent nitration acid is normally processed to purify and recover nitric and/or sulfuric acid. Recovery is incorporated into the nitric acid concentration (NAC) process, with spent nitration acid being bled into the dehydration step along with weak nitric plus concentrated sulfuric acid. Since nitration acid is a mixture of concentrated sulfuric and nitric acids, separation of sulfuric and recovery of nitric acid occurs, where practiced, in the NAC step, and recovery of spent nitration acid will be discussed as part of the NAC process. At Holston AAP only, concentrated nitric acid is mixed with liquid anhydrous ammonia to produce nitric acid/ammonium nitrate, used in HMX and RDX manufacture (3f). Unlike the commercial explosives industries, where ammonium nitrate is a commonly manufactured and used explosives intermediate, the Holston AAP manufacturing process for HMX and RDX represents the only current military production of ammonium nitrate.

23. Waste Sources

a. In the AOP process, a mixture of ammonia gas and air is combusted in the presence of a catalyst to produce nitric oxide plus water. The gaseous products are cooled and excess air added to convert nitric oxide to nitrogen dioxide. The water formed in the ammonia oxidation step reacts with nitrogen dioxide, producing nitric acid and nitric oxide. Cooling and condensing results in the formation of dilute (50-60%) nitric acid, which is sent to nitric acid concentration. The nitric oxide produced in the final reaction is again oxidized by excess air to nitrogen dioxide, which is converted to dilute nitric acid by aqueous scrubbing in countercurrent adsorption towers.

b. Wastewaters from AOP facilities include cooling water and leakage, and water used for clean-up of spills, floors and equipment. Because AOP process effluents are normally mixed with large volumes of cooling water, and frequently combined with wastes from NAC and sulfuric acid processes, it is difficult to specify the pollutant discharge solely associated with AOP operations. In general the AOP effluents are low in pH and high in nitrate content, with low to moderate ammonia levels (8f).

Flow data from the Holston AOP facility are summarized in Table 11. Approximtely four percent of the total flow is process effluent. Based upon the data of Table 11, 508 lbs/day of ammonia are discharged. This is equal to about 40 mg/l in the combined flow, assuming no contribution from floor washdown. Approximately 250 lbs/day nitrate discharge is reported for the Joliet AAP ammonia oxidation process (8c). This is equivalent to about 4000 mg/l nitrate for the AOP process effluent alone, at a process flow of 12.3 gpm (17,760 gpd). Beyond the expected acidic pH, no other wastewater characterization data specifically related to AOP operation are available. However, the above cited data indicate that AOP process effluent will contain appreciable quantities of nitrate and ammonia nitrogen.

c. The standard nitric acid concentration (NAC) operation is a continuous process in which dilute nitric acid is distilled in the presence of sulfuric acid. The sulfuric acid acts as a dehydration agent. Concentrated (98%) nitric acid is condensed from the distillation vapor, and diluted sulfuric acid is removed, normally for reconcentration in on-plant sulfuric acid concentration (SAC) facilities. Holston AAP uses a modification of this process, wherein 61% nitric acid is concentrated by mixing with a hot solution of 72% magnesium nitrate (made by dissolving magnesium carbonate in nitric acid), which acts as the dehydrating agent. The concentrated nitric acid is removed as vapor, condensed, cooled and stored. The diluted magnesium nitrate is recovered, reconcentrated and reused. Wastewaters from NAC processes orginate from acid spills, floor washings and cooling water (8f).

d. Except for Holston AAP, there are essentially no process-specific wastewater characterization data available for the NAC process. The applicability of the Holston data, which is based upon magnesium nitrate dehydration rather than the more common sulfuric acid dehydration process, is questionable for extrapolation to NAC wastes at AAP's operating sulfuric acid-based NAC facilities. Data from Holston AAP indicate a flow of about 9000 gpm of contaminated process water, with a cooling water and steam condensate flow of 1.4 MGD at a production rate of 51 TPD* nitric acid (1d(2)). Waste characteristics of the combined flow are summarized in Table 12. For comparison with the Holston process flow, Newport AAP is reported, when in operation, to have a process wastewater flow of only 10 gpm from its nitric acid concentration and recovery units (3f). Waste characteristics are not reported. However, for Newport and other AAP's utilizing sulfuric acid in their NAC facilities, sulfate plus contaminants present for Holston AAP (Table 12) would be anticipated.

e. Because of the lack of available data on process effluent from either AOP or NAC facilities, it is difficult to define the levels of contaminants. There are data available, however, on combined flows from AOP plus NAC operations. Combined process wastewater data are

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*tons per day

Table 11. Holston AAP Wastewater Volumes (1d(2))

Source	Volume, gpd	Comments
1. Ammonia Purge Pot Blowdown	46,000	Approximately 88 lbs/day NH_3.
2. Ammonia Vaporizer Blowdown	not measured	Approximately 420 lbs/day NH_3.
3. Adsorption Column Blowdown	not measured	Approximately 112 lbs/day HNO_3.
4. Adsorption Column Demister Blowdown	5-7	pH 0.1, TOC 28 mg/1, COD 95 mg/1, NH_3-N 37.2 mg/1, NO_3 + NO_2-N 100,000 mg/1.
5. Floor Washdown	1,440	
6. Steam Condensate	7,554	
7. Cooling Water	1,439,000	
Total, gpd	>1,494,000	
Cooling Water, %	<96.3	
Process Waste, %	>3.7	

Note: Production rate of 200 TPD equivalent 100% nitric acid.

Table 12. Wastewater Characteristics of Holston AAP Magnesium Nitrate-Based NAC Process (1d(2))

Parameter	Average	Range
Flow, MGD	1.8	0.9-2.8
pH	6.3	3.0-8.2
Total Solids, mg/l	603	480-876
Susp. Solids, mg/l	7.1	4.0-12.7
COD, mg/l	36	16-51
TOC, mg/l	6.8	6-8
NH_3-N, mg/l	0.5	0.2-1.6
NO_2 + NO_3-N, mg/l	29	12-60

presented in Table 13. Similar (averaged) data for commercial explosives plants are also included in Table 13, for comparison. There is a great deal of variability in the data of Table 13, due to variation in extent of dilution of process effluents with cooling water, among other factors. The data suggest however that the most significant wastewater characteristics are low pH, with high ammonia and nitrate nitrogen, and high sulfate levels.

f. At Joliet AAP, a Direct Strong Nitric Acid (DSNA) process has been constructed and is undergoing start-up. This new process will replace the existing AOP/NAC facility at Joliet. The DSNA process will produce both weak and strong nitric acid, in a single operational sequence, without the use of sulfuric acid (8f). Although there is no wastewater information on the new process, it is claimed to be a much more pollution-free facility than the present AOP and NAC facilities at Joliet AAP. Major wastewater flows will be cooling tower and boiler blow-down, clean-up water and regenerant brine from water demineralization units (8c, 8f).

24. Effects of Water Management

a. Two areas of water management are under consideration for AOP/NAC facilities. These are: separation of cooling water from process effluent; and use of process effluent from NAC facilities as water source for both nitric acid production and NO_2 abatement. Based upon the data of Table 11, approximately 96 percent of the total AOP discharge at Holston AAP is cooling water. Separation of this flow would reduce the process contaminated effluent from 1028 to 38 gpm. Similarly, whereas the Holston NAC facility has a combined discharge of 1250 gpm (Table 12), the modern Newport NAC with flow segregation has a process effluent of 10 gpm (3f). Thus, for existing AOP/NAC facilities, flow segregation will result in a major reduction in the volume of wastewater to be handled. Use of the new DSNA process at Joliet AAP is expected to eliminate process effluent (8f).

b. The use of process effluent for the NAC facility at Holston AAP, as a water source for nitric acid production and NO_2 abatement, has been suggested (1r(1)). Advantages for this reuse concept include a 59 percent reduction in nitric acid discharge, and economic benefits through acid recovery and reduced waste treatment costs. Possible obstacles to implementation include lack of demonstrated application, and requirements imposed by physical-chemical manufacturing systems presently in use, safety, and product quality requirements (1r(1)). The potential benefits that would result from effluent use however indicate that serious consideration should be given to the application of this concept.

25. Current Treatment Practice

a. Table 14 summarizes treatment now employed at AAP's for AOP/NAC facility wastes. At all plants except Newport, the wastewater

Table 13. Comparison of Characteristics of Combined Wastewaters from AOP plus NAC Facilities

Parameter	Joliet AAP		Radford AAP (3f)	Holston AAP (5a)	Commercial Explosives Plants (4d)
	Areas 1 & 2 (3f)	Area 3 (8f)			
Flow, MGD	21.2	11.2	na	3.9	0.49
pH	7.2	2.7	na	na	2.3-3.1
BOD, mg/1	na	<10	13	7.2	13.5
COD, mg/1	na	40	46	19.4	208
NH_3-N, mg/1	na	na	1.2	0	191
NO_3 + NO_2-N, mg/1	26	6.8	163	94	206
Sulfate, mg/1	373	320	na	na	312

Numbers in parenthesis are reference sources.

Table 14. Current Treatment Practices at AOP/NAC Facilities (3f)

Location	Current Treatment
Holston AAP	No treatment.
Radford AAP	Equalization, neutralization with soda ash for spent TNT nitration acids. Neutralization with lime for acid plant wastes, and sludge sedimentation.
Joliet AAP	Neutralization.
Badger AAP	Neutralization with lime, aeration.
Newport AAP	Neutralization with lime. Calcium sulfate sludge sedimentation.
Volunteer AAP	Neutralization with lime. Calcium sulfate sludge sedimentation.

is predominately cooling water, contaminated with a much smaller flow of process effluent. Current practice ranges from no treatment (Holston), to neutralization, and at three plants calcium sulfate sludge removal. Where treatment is applied, it is thus restricted to pH adjustment plus partial sulfate removal by precipitation of calcium sulfate. The precipitation of calcium sulfate is limited to those process wastewaters high in sulfate. Since AOP/NAC wastes have low to moderate sulfate levels (Table 13), calcium sulfate precipitation would be minor except in the presence of wastewaters representing a combination of AOP/NAC effluents and high sulfate (e.g. SAC) wastes. In that instance, calcium sulfate precipitation would be most effective on the high sulfate stream alone, rather than a combined waste stream.

b. Where treatment is employed, acceptable effluent levels appear to result directly from process effluent dilution, rather than application of good treatment technology. For example, neutralization at Radford AAP is reported to be inadequate, with wide fluctuations in the effluent pH and poor solids removal in the settling lagoons (4c). However, the (diluted) discharge is reported to have an average pH of 8.6 and average suspended solids of 1.2 mg/l (3f). Joliet AAP reports an effluent pH of 7.2 from Acid Areas 1 and 2, with a total combined flow of 20 MGD (3f). Acid Area 3 pH ranges from 2.6 to 9.7, with a flow of 11.2 MGD (3f). Combined flow from Badger AAP ranges in pH from 1.8 to 11.5, with an average flow of 29 MGD. Nitrate and sulfate discharge for this plant-wide combined discharge were 16-105 (72 average) and 225-600 (426 average) mg/l, respectively (3f).

c. Volunteer AAP uses a feed-forward/feed-back pH control system, through three sequential treatment ponds, for neutralization and suspended solids removal. The system appears effective for pH control, with acid area wastewater (AOP, NAC, SAC and Oleum manufacture) being adjusted from pH 3 to 6.9 by addition of lime through the system. Neutralization plant effluent ammonia, nitrate plus nitrate nitrogen, and sulfate, are reported to be 1.9, 12.5 and 350 mg/l (1r(1)). Effluent calcium is 177 mg/l, reflecting the high lime dosages used in neutralization, although total dissolved solids are only 767 mg/l. Based upon the performance of the Volunteer AAP neutralization system, effective pH control is possible. Other AAP's however provide less effective control, and consequent inadequate neutralization. In no instance is nitrogen or rigorous sulfate pollution abatement employed.

26. Modifications to Current Treatment

a. Treatment modifications currently under consideration for five AAP's are listed in Table 15. In all except two instances (Joliet and Volunteer AAP's), no provisions for nitrogen or sulfate control are scheduled. At Joliet AAP however, essentially complete deionization is under consideration (8c). Proposed modifications thus represent a full spectrum from continuation of neutralization but no control of other constituents, to removal of all suspended and dissolved pollutants.

Table 15. Proposed Modifications to Current Treatment

Location	Modification	Reference
Holston AAP	Aerated treatment ponds.	3f
Radford AAP	Improved neutralization, and removal of calcium sulfate sludge.	3f
Joliet AAP	Sulfate removal by calcium and barium precipitation; nitrate and ammonia removal by ion exchange.	8c
	Reduction in process effluent by substitution of DSNA for AOP/NAC facilities.	15zb
Badger AAP	Improved neutralization.	3f
Newport AAP	Neutralization, and calcium sulfate sludge removal.	3j
Volunteer AAP	Lime neutralization, clarification and filtration. Filter cake to be landfilled. Residual nitrate and sulfate to be treated by ion exchange.	15zp

b. Holston AAP combined wastes, including nitric acid process effluents, are scheduled to be treated in aerated biological waste treatment ponds (3f, 4a). Flows from the nitric acid area contain low values of BOD and COD. Other constituents such as nitrate and sulfate will not be affected by pond treatment. Ammonia nitrogen might possibly be biologically oxidized to nitrite or nitrate, depending upon the lagoon design and mode of operation. However, aside from the small amount of BOD, and possible ammonia nitrification, the major pollutants (nitrate and sulfate) will not be reduced or eliminated in aerated pond treatment. Because of this limitation of biological treatment, a recent EPA review of Holston AAP recommended: (1) steam stripping of ammonia-rich waste stream prior to pond treatment; (2) second stage polishing treatment of the pond effluent by activated carbon or some similar physical or chemical means; and (3) biological denitrification of the second stage effluent for nitrate control (4a). Sulfate removal was not discussed. Alternatives to the EPA proposal are discussed and evaluated in paragraph 27.

c. Radford AAP proposes to modify the present neutralization facility, which now employs soda-ash, by: providing equalization tanks; additional neutralization tanks for longer retention time and better mixing; switching to lime neutralization; and providing calcium sulfate sludge removal facilities (6a). The treatment system modifications should result in improved pH control, but little sulfate and no nitrate control. Implementation of more rigorous treatment was apparently discouraged as a result of the regional U. S. EPA office indicating satisfaction with neutralization only at Radford AAP, through 1977 (15y).

d. A new neutralization and ion exchange plant has been constructed at Volunteer AAP, to handle wastes from the acid manufacturing facilities (3f). At Badger AAP, the new acid waste treatment facility is limited to neutralization, and aeration to increase dissolved oxygen levels (3f). Treatment at Newport AAP will be limited to neutralization, with calcium sulfate sludge separation (3j). There is no provision for eliminating nitrate, nor reducing sulfate below the solubility of calcium sulfate, at either of these two AAP's. At Newport, neither the present system, nor any proposed MCA* projects, will provide sufficient treatment to satisfy the plant's present discharge permit (3j).

e. Pollution abatement plans for the plants cited above are in distinct contrast to the proposed treatment system for Joliet AAP. At Joliet, a $2.5 million waste treatment facility has been proposed, which incorporates two-stage lime neutralization with calcium sulfate sludge removal, barium carbonate treatment to precipitate residual sulfate as the barium salt and calcium as the carbonate salt, followed by cation/anion exchange treatment to produce demineralized water for reuse. Anion regenerant will be concentrated by evaporation, and sold as an agricultural fertilizer material. Cation regenerant (dilute sulfuric acid) will be treated by the sulfate removal process described above (8c). Nitrate removal will occur in the anion exchange process. Waste ammonia streams will not be handled in this proposed system, although the cation exchanger should remove any trace ammonia present. The consultant engineering firm which developed the concept design for the Joliet system has recommended pilot testing the ion exchange system, as well as an alternative biological denitrification process (8c).

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*Military Construction-Army

27. Alternatives to Current Practice

a. The four parameters of wastewaters from nitric acid manufacture and concentration which are likely to require control are pH, ammonia-nitrogen, nitrate-nitrogen, and sulfate. Current practice, particularly at Volunteer AAP, demonstrates that proper treatment facility design and operation can achieve effective neutralization. Treatment techniques and costs for pH control are equivalent to those well established for other industry wastewaters (4d). The control of sulfate, resulting from the use of sulfuric acid in NAC facilities, will be discussed in the following (sulfuric acid) section of this chapter. The discussion in this section will therefore be restricted to control of ammonia and nitrate.

b. Biological treatment for both ammonia and nitrate appears to be an effective and acceptable type of treatment for munitions wastes, providing that the wastewaters do not contain toxic materials at biologically harmful levels. Although most research on bionitrification of ammonia has been directed toward wastewaters containing less than 60 mg/l NH_3-N, limited work on more concentrated wastewater has proven bionitrification to be effective. Recent data on bionitrification processes are summarized in Table 16. These data suggest that while the activated sludge process is an effective nitrification process at moderate ammonia levels, it is much less effective than either the oxidation ditch or rotating disc for high ammonia levels. The feasibility of ion exchange or other physical-chemical methods of ammonia control has also been proven (16ze, 16zf), although the high nitrate levels in military munitions wastewaters indicate that a combination of biological nitrification-denitrification is likely to be the treatment method of choice.

c. A great deal more effort has been directed toward assessment of nitrate control technology than for ammonia. Table 17 summarizes the results of preliminary feasibility studies performed by the Army on nitrate control technology, and indicates that on the basis of proven treatment technology plus costs, biodenitrification is likely to be the method of choice. However, recent developments in ion exchange and reverse osmosis technology, together with the prospect of valuable product recovery, indicate that serious consideration should be given to these alternatives. In the commercial explosives industry, evaporative ponds and spray irrigation have found wide acceptance (4d). However, restrictions imposed by climatological factors, land availability, nature of terrain, and volumes of wastewater indicate that these latter two alternatives may not be feasible for the military munitions industry.

Table 16. Ammonia Bionitrification Processes and Performance Data

Process	Detention Time	Ammonia - N, mg/l		Percent Nitrification	Reference
		Influent	Effluent		
Activated Sludge	10.7 Hr.	24.5	1.0	96+	16za
	11.5 Hr.	92.0	1.0	99+	
Activated Sludge	4.5-6.5 Days	600	138	77	16zb
	6.5-8.5 Days	600	72	88	
Oxidation Ditch	2.0 Days	577	5.0	99+	16zc
Rotating Disc	1.5 Days	785	2.3	99+	16zd
	2.0 Days	880	1.5	99+	
	3.0 Days	790	1.7	99+	

Table 17. Summary of Nitrate Treatment Methods (3d)

Method	Removal Efficienty, %	Approx. Cost, $/MG
Biodenitrification	70-95	3.45-30
Algae Harvesting	50-90	20-35
Ion Exchange	80-99	170-300
Electrodialysis	30-50	100-250
Chemical Reduction	33-90	-
Reverse Osmosis	50-96	100-600
Distillation	90-98	400-1000
Land Application	5-15	na

d. Of the three remaining nitrate treatment processes, biological denitrification has been most intensively studied. Most of those investigations have been directed toward removing nitrate from municipal wastewaters (4e). The U. S. Army has carried out pilot scale suspended growth biodenitrification studies at two of its contractor operated munitions plants (3d). Initial studies at Sunflower AAP indicated that detention times exceeding, ten days were required for 90 percent or greater nitrate reduction, at suspended solids levels of 100-200 mg/l. A modified 5000 gpd pilot unit tested at Radford AAP, and operated at 1000-3000 mg/l suspended solids, is reported to have achieved 93 percent denitrification with an 18 hour detention time. Average influent NO_3-N of 558 mg/l was reduced to 47 mg/l effluent concentration. At influent NO_3-N concentrations below 400 mg/l and suspended solids below 1400 mg/l, the process yielded effluent nitrate levels of 1 mg/l, however (3i). The primary disadvantages of the biodenitrification process are the need for close pH and temperature control, and the large quantities of methanol required. At a nitrate level of 500 mg/l, about 5 tons of methanol is required per million gallons of waste treated (3f).

e. The recent development of anaerobic packed and suspended growth bed columnar type biodenitrification processes is promising, insofar as reduction in treatment time required. Pilot studies with a 26 gpm pilot suspended growth system have resulted in nitrate reduction from 21.5 to 0.2 mg/l, representing 99 percent denitrification at a detention time of only 6.5 minutes (16zg). Studies on a similar system using a munitions wastewater containing approximately 100 mg/l nitrate nitrogen and with a 152 minutes detention time resulted in 98.9 percent nitrate removal (16zh). Preliminary results such as these for high rate biodenitrification indicate that this process, by improving process reliability and reducing required treatment time, may replace activated sludge type denitrification as the preferred method. Pilot biodenitrification studies in an upflow column are programmed to be performed at Badger AAP (15y).

f. Ion exchange treatment for nitrate removal has been largely limited to the abatement of low nitrate concentrations (16zi-16zk). One historical problem with the use of ion exchange for nitrate treatment has been the lack of resin specificity for nitrate. However, nitrate selective resins have recently become available (4f, 16zl). The only reported ion exchange system in full-scale use for the treatment of high nitrate concentrations is the Chemical Separation Corporation Continuous Counter-Current (Chem-Seps) Ion Exchange System (3d). This system has been installed at the Farmers' Chemical Association, Inc. plant (Tyner, Tennessee), a manufacturer of ammonium nitrate. The system is reported to reduce nitrate levels of 1230 mg/l at 0.9 MGD, to effluent concentrations of 7-11 mg/l, in the presence of other ions. The regenerants used are nitric acid and ammonium hydroxide, with ammonium nitrate (concentration about 19%) being recovered in the resin regeneration step.

g. Radford AAP has assessed the selectivity of other resins, including liquid amine exchangers, for nitrate (3d). Of ten resins studied, the liquid exchangers LA-1 and LA-2 (Rohm and Haas Co.) were found to be most selective for nitrate removal, without concurrent sulfate removal. Nitrate removal without concurrent sulfate removal was desired, in order to obtain a purer regenerant. However, the kerosene solvent used with the liquid exchangers was felt to represent a possible contaminant of the regenerant by-product which, if reused could result in a potentially hazardous explosive mixture.

h. The application of the Chem-Seps process for munitions facilities appears feasible, particularly at Holston AAP, which uses ammonium nitrate as an intermediate in HMX/RDX manufacture. The Chem-Seps process, in addition to nitrate removal, is reported to reduce NH_3-N levels from 340 to 2-3 mg/l. The sulfate level of the waste being treated was only 72 mg/l (16zm), and it is possible that the higher sulfate levels associated with explosives wastewaters may interfere with effective nitrogen removal. However, preliminary studies on the Chem-Seps System by the Army indicated reduction of nitrate from 1650 to 20 mg/l, even in the presence of high sulfate concentration (3i). This process, using DOWEX Resin MWA-1, also reduced sulfate from 4320 to 200 mg/l, The process, for a 3 MDG flow, is estimated to require a capital investment of $1,650,000 (3i).

i. Although there is some apparent reluctance to using a nitrate treatment process which yields a fertilizer material, and which would require the military to market the regenerant as a fertilizer, ion exchange undoubtedly represents the best and most reliable nitrate treatment process which has been proven in full-scale use. Serious consideration is now being given by the Army to use of systems such as the Chem-Seps process, particularly if improved control of manufacturing operations can reduce sulfate levels in the nitrate-rich wastewater (15y). Indeed, the concept design of the acid waste treatment facility at Joliet AAP incorporates such a system (8c).

j. If the acid waste can be concentrated to about 15 percent, reverse osmosis is a technique by which recovery would be feasible for acid reuse in the plant (3i). At the present time, application of reverse osmosis is largely limited to desalination and production of drinking water, and recovery of products in the food processing and electroplating industries (16zn). Investigations of reverse osmosis as a method of concentrating nitrate wastes are few, and those reported in the literature indicate variable results (16zm, 16zo). Advantages of reverse osmosis include its low energy requirement and corrosion free operation, in contrast to evaporative systems. However, reverse osmosis membranes are affected by pressure, chemical change and hydrolysis, temperature and surface coating (16zp).

k. The Army has investigated on a pilot scale reverse osmosis treatment of nitrate wastewaters. At pH 1.5, no nitrate removal occurred although 99 percent sulfate removal was achieved. Nitrate removal efficiency increased with increasing pH, to 90 percent at pH 7.0. Sulfate removal was not found to be pH dependent, with reverse osmosis achieving 99 percent sulfate separation at all pH values tested. However, it appears that the lower limit of osmosis treatment is near 20 mg/l NO_3-N, and that achieving lower concentrations would not be economically feasible. Reverse osmosis application thus appears to be best suited for nitrate recovery, with subsequent treatment of the dilute permeate by other means such as biodenitrification or ion exchange. The Army is continuing to investigate reverse osmosis, utilizing low-pH resistant sulfonated polyphenylene oxide (SPPO) membranes, with evaporative concentration of the process brine to recover mixed nitric and sulfuric acid for reuse. This process, if proven feasible, will both eliminate the need for neutralization and provide product recovery.

l. While reverse osmosis must still be considered as being in the developmental stage, two other proven technologies are available which can provide effective nitrate control. On the basis of economics only, biological denitrification would be the method of choice, while on the basis of process reliability and prospect of by-product recovery ion exchange is most promising. With proper process design and good control, either technology should achieve effective nitrate removal.

28. Impact of Air Pollution Control

Significant levels of nitrogen oxide are emitted from AOP and nitric acid plants (3f). At some plants these emissions are not controlled, although EPA emission standards have been promulgated for nitric acid plants. Thus, control technology must be implemented at the military nitric acid facilities. Where controls are in use, such as for NAC emissions from Holston AAP, they are typically rather ineffective scrubber systems (3f). Newport and Volunteer AAP AOP's use catalytic combusters, designed to reduce nitrogen oxides to below 200 ppm (3f). Nitrogen oxide control procedures under consideration by the military include: new AOP and DSNA production facilities which would reduce emissions; incineration; sulfuric or nitric acid scrubbing with recovery; catalytic reduction; and dry (molecular sieve) absorption (16zq). None of these control techniques generate water pollution, and there is thus no expected impact from air pollution control on water pollution from nitric acid manufacture or concentration.

29. Summary

a. Despite the lack of reliable wastewater characterization data for process effluents of AOP and NAC facilities, there is sufficient evidence to establish that the effluents are of low pH, with high ammonia and nitrate levels for both the AOP and NAC processes. The latter process effluent also contains moderate to high sulfate levels, due to the use of concentrated sulfuric acid as a dehydrating agent.

b. Technology for control of pH, ammonia and nitrate is well established. However, among military munition and propellant plants there is much inconsistency in the extent of waste treatment utilized or planned. Volunteer and Joliet AAP's propose a full spectrum of treatment, including neutralization, sulfate removal by precipitation or ion exchange, and nitrogen removal by ion exchange. Other plants, with equivalent wastewaters, propose only neutralization, perhaps accompanied by some minor degree of sulfate control through lime treatment, with calcium sulfate precipitation. The discrepancies in levels of treatment to be implemented indicate that no consistent effluent standards have been established by the Military. In the absence of definition of such standards by either the military or the U.S. Environmental Protection Agency, the paradoxical spectrum of treatment levels programmed will likely continue.*

*Note added in press. Interim/Final guidelines for Explosives Point Source Category were issued in the Federal Register, Volume 41, No. 47, pp 10180, March 9, 1976.

SECTION III-C - SULFURIC ACID - MANUFACTURE, CONCENTRATION AND RECOVERY

30. Introduction

a. Sulfuric acid is manufactured, and concentrated to oleum, for use as a dehydration agent in the nitric acid-based nitration of products such as TNT and nitroglycerin. In most instances, the spent nitrating acid mixture is processed for recovery of both nitric and sulfuric acids. In some instances the recovered sulfuric acid is concentrated and sold commercially, as at Radford AAP, while at other plants the recovered acid is regenerated and reused. Military munitions plants which recover sulfuric from spent nitrating acids are Radford, Joliet, Badger, Newport and Indiana AAP's. Recovered sulfuric acid is a by-product of the NAC process described in the preceding section of this chapter.

b. In the sulfuric acid concentration (SAC) process, dilute sulfuric acid yielded from the NAC operation is concentrated to 93% by evaporation. Plants operating SAC processes include Radford, Joliet, Badger, Volunteer, Newport and Indiana AAP's. This concentrated acid is used to produce oleum at the first four named AAP's above. In oleum manufacture, spent sulfuric acid is decomposed and elemental sulfur is oxidized to sulfur dioxide, then catalytically oxidized to produce sulfur trioxide gas. The gas is absorbed with concentrated sulfuric acid in absorption towers, to yield 30-40% oleum. This is the new sulfuric acid regeneration (SAR) process. The SAR process produces oleum directly, plus sulfuric acid of different concentrations, 98% sulfuric acid being the weakest.

31. Waste Sources

a. Process waste sources, in addition to the NAC-based sulfuric acid recovery operation described previously, are the SAC and oleum facilities.

b. Wastewaters from the SAC process originate from occasional acid spills, floor washings and water used for cooling (8f). Wastewater generated in oleum production consists mainly of cooling water, contaminated by acid spills. At Joliet, an additional waste source is acid tank car drainage and washout (8f). The major wastewater from the SAR process is a weak (2.5%) sulfuric acid solution, which results from cooling and scrubbing of combustion products (3f, 8f). At Newport AAP this flow is reported to total 180 gpm (3f). Waste characterization data for SAC, oleum and SAR facilities are limited. Table 18 summarizes available data. The oleum facility at Joliet AAP is no longer in use. Oleum is currently purchased from an outside source, pending start-up of the new SAR facility.

c. The wastewaters from all except tank car clean-up are predominantely cooling waters, which result in high dilution of process contaminated effluents. The major characteristics expected for the process effluents from SAC, oleum and SAR facilities would be low pH and high sulfate levels.

Table 18. Waste Characteristics of Sulfuric Acid Manufacture and Concentration

Parameter*	Oleum Production				Tank Car Clean-up (1g(3))
	Joliet (8f)	Joliet (1g(3))	Joliet (3f)	Radford (3f)	
pH	6.8	7.8	2.3-9.8	-	7.6
COD	30	-	-	51	-
BOD_5	10	-	-	12	-
Nitrate-N	7.7	-	31	2.4	-
Ammonia-N	-	-	-	0	-
Kjeldahl-N	-	-	-	0.3	364
Sulfate	153	133.4	153	-	5875
Suspended Solids	44	-	-	4	73.5
Tot. Dissolved Solids	484	-	-	274	6401

*All parameters mg/1, except pH.

32. Current Treatment Practice

a. Treatment of wastes associated with sulfuric acid manufacture and concentration is, at present, restricted to pH control by neutralization with lime or soda-ash. The waste is frequently combined with wastewaters from AOP/NAC facilities, prior to neutralization. At Radford AAP, SAC wastewater is treated together with wastes from TNT production facilities and a red water incineration unit, by soda-ash addition. Oleum wastewater is treated at a separate neutralization facility, also with soda-ash (4c). The combined TNT/SAC effluent from the first neutralization facility is reported to be adequately neutralized (4c). For a combined wastewater flow of 0.16 MGD from the neutralization pond, the effluent averages 2167 mg/l sulfate, with a maximum of 3128 mg/l (3f). The oleum wastewater treatment facility (4.2 MGD) has been cited as performing inadequately insofar as pH control, and has an effluent sulfate concentration of 47 mg/l (4c).

b. At Joliet AAP, treatment is restricted to neutralization of acid spills (3f). Badger AAP discharges oleum wastewater to an evaporation/percolation pond, without pretreatment. Wastewaters from the SAC facilities are treated with lime, for neutralization, as is the SAR wastewater at Newport AAP and SAC/oleum effluents at Volunteer AAP. Like Radford, Volunteer AAP has been cited for poor pH control (1r(1)).

c. There is no question that proper technology is available and can be implemented for pH control (4d). There is at present, no effort directed toward sulfate control, although sulfate may in fact be reduced to some extent in those plants utilizing lime for neutralization, as a result of calcium sulfate precipitation. Calcium sulfate is a relatively soluble salt however, as shown in Figure 8, which relates effluent calcium to effluent sulfate concentration, on the basis of a theoretical molar solubility product of 2.4×10^{-5} (16zr). This relationship predicts effluent sulfate levels exceeding 1000 mg/l, for effluent calcium concentrations below 90 mg/l.

33. Modifications to Current Treatment

a. Modifications which have been proposed for existing treatment facilities, to improve sulfate control, include calcium and/or barium sulfate precipitation at Volunteer and Joliet AAP's, and multiple-effect evaporation for acid waste concentration and recovery at Badger, Radford and Sunflower AAP's (3i). At Newport, and apparently other plants, no specific sulfate removal technology is under consideration. Newport AAP will use lime neutralization, which provides partial sulfate precipitation. However, the proposed treatment will not satisfy the effluent sulfate requirement of Newport's present NPDES permit (3j).

b. The most comprehensive treatment system is that proposed for Joliet AAP. It is to consist of calcium and barium sulfate precipitation, followed by ion exchange treatment (8c). The solubility of barium sulfate is much less than calcium sulfate, as shown in Figure 8. Barium is a toxic metal, and ion exchange will serve both to remove barium

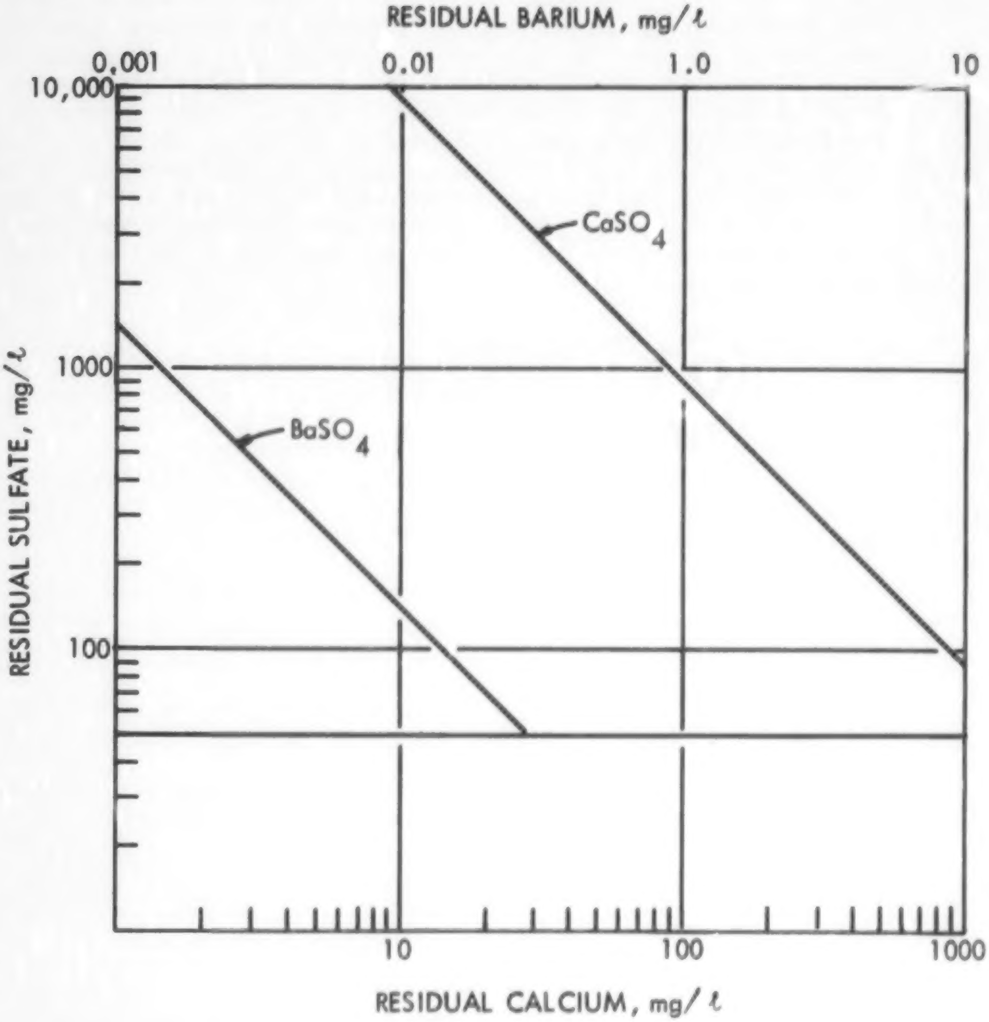

Figure 8 - Solubility of Calcium Sulfate, $K_{sp} = 2.4 \times 10^{-5}$ (16zr)

Solubility of Barium Sulfate, $K_{sp} = 1.1 \times 10^{-10}$ (16zs) from the precipitation effluent, and to remove other trace constituents. The specific steps of the proposed Joliet treatment system are: two-stage neutralization with lime, resulting in formation of calcium sulfate sludge; addition of barium carbonate to form mixed barium sulfate and calcium carbonate sludges; and ion exchange for effluent from the precipitation processes. Sludges will be stored in lined lagoons. The first step in ion exchange treatment is to be the cation unit, which will be regenerated with dilute nitric or sulfuric acid. This regenerant will be treated with other acid wastes, as described above. Effluent from the cation unit will be treated by anion exchange, on the hydroxide cycle. Regeneration will be ammonium hydroxide, with regenerant partially evaporated to yield fertilizer feedstock containing 45 percent ammonium nitrate. The deionized effluent will be used for boiler feed and other plant water needs (8c).

34. Alternatives to Current Practice

a. Methods proven feasible for sulfate treatment, including those described above, include:

(1) Reverse Osmosis - Separation of sulfate from the wastewater by use of suitable membranes, to produce water for plant reuse and concentrated brine for reclamation processes.

(2) Ion Exchange - Removal of sulfate by use of sulfate specific resins, producing reclaimed water and a useful by-product resulting from the regeneration of the ion exchange bed.

(3) Evaporation - Combined use of reverse osmosis or ion exchange and evaporation techniques to recover sulfuric acid.

(4) Precipitation - Reduction in sulfate by use of lime and/or barium to produce calcium and barium sulfate precipitate.

(5) Calcination - Produce calcium sludge by precipitation with lime, followed by high temperature calcination to evolve sulfur dioxide for sulfuric acid production, plus lime recovery.

b. Reverse osmosis has been investigated at pilot scale, in combination with nitrate removal. High sulfate removal efficiencies (99+%) are reported even at acidic pH. Permeate sulfate levels of below 100 mg/l can be achieved, with brine sulfate levels above 4000 mg/l (31). However, membrane hydrolysis at low pH greatly decreases useful membrane life. In the absence of more resistant membranes, neutralization would likely be required for the reverse osmosis feed stream. This may result in precipitation, and fouling of the membrane by solids. Limited experiments with acid resistant sulfonated polyphenylene oxide (SPPO) reverse osmosis membranes have indicated good performance however, and may enhance the feasibility of reverse osmosis treatment.

c. The most technically feasible method of sulfate treatment appears to be precipitation. However, the solubility of calcium sulfate is high (Figure 8), and lime treatment may not be feasible for more stringent effluent requirements. The use of barium to precipitate sulfate has been proposed (8c), but cost and the possibility of exceeding effluent barium levels appear to be major disadvantages.

d. The economic and technical difficulties associated with treatment for pollutants such as nitrate and sulfate has led to several applications of waste disposal by land irrigation, in the commercial explosives industry (4d). The use of land application appears practical where suitable soil and climatic conditions exist. The soil has the inherent ability to be able to remove materials from the wastewater by both microbial and crop utilization, and by physical adsorption. However, only the biological processes affect the nitrates since the soils, which are generally negatively charged, allow the nitrate to pass unimpeded, depending upon the hydraulic loading rate (3d). Limitations include the large land area required, and the possibility of contamination of ground water.

35. Impact of Air Pollution Control

Both SO_x and sulfuric acid mist emissions result from sulfuric acid and oleum plants and SAC facilities (3i). Control procedures under study include demisters, molecular sieves, catalytic reduction and scrubbing. All processes incorporate recovery, with the catalytic reduction process yielding elemental sulfur. One scrubber process uses glycol as an absorption medium, from which SO_2 is recovered with glycol being recycled. The molecular sieve process demists stack gases and adsorbs the contained SO_2. The sieve bed is cyclically regenerated, with the effluent recycled for conversion to sulfuric acid (3f). There is no apparent water pollution impact from proposed air pollution control procedures now under consideration. Volunteer AAP utilizes Mahon fog filters to remove acid mist from sulfuric acid recovery of TNT nitrating acids (3f). This wastewater, which is acidic and high in TNT, nitrate and sulfate, can be handled by standard wastewater treatment procedures described in this chapter.

36. Summary

a. As in the case for nitric acid production, there is inadequate information available to accurately characterize process effluents from sulfuric acid facilities. Noteworthy aspects of the effluents include low pH and high sulfate levels. Several acid plants have been cited for improper pH control. The technology of pH control is well established, and there seems to be no technical reason why these plants cannot achieve effective control, other than from lack of commitment of resources to the problem.

b. Similarly, methods of control of sulfate have been sufficiently well established to allow at least two plants (Volunteer and Joliet AAP's) to reach the design stage for sulfate abatement. Other plants, however, anticipate at best only minor sulfate control, through precipitation resulting from lime addition for pH control. While effective, available control methods are either costly or yield by-product sulfate brine or sludge. Additional research on methods of sulfate control is warranted. The impetus for sulfate control must originate from a national requirement, if all sulfuric acid facilities are to meet the levels of performance projected for Joliet and Volunteer AAP's.

SECTION IV - NITROCELLULOSE

37. Introduction

a. Nitrocellulose is currently manufactured at Radford and Badger AAP's by a batch process. A continuous process has been developed and is being installed at Radford AAP. Indiana and Sunflower AAP's also have capability for nitrocellulose production, but are not currently manufacturing this product (2b). Between 30 and 40 lb of dry, fluffed cellulose (cotton linters or wood pulp) is the normal batch size. This is submerged in about 1600 lbs of mixed (nitric plus sulfuric) nitrating acid. The composition of the mixed acid is adjusted to the grade (nitrogen content) of nitrocellulose required. The nitration reaction is exothermic, and the charge temperature is kept below 37-40°C by cooling.

b. After about 25 minutes in the nitrator, the charge is transferred to a centrifuge, where spent acid is removed, and the nitrated cellulose is washed in a large excess of water. The spent acid is pumped to a tank, where a portion is fortified for reuse and the remainder is sent to acid recovery. The crude nitrocellulose is usually pumped as a water slurry to the purification area, where it goes through an elaborate series of water washes, boiling treatments, neutralizations and heating steps to stabilize the nitrocellulose (NC).

c. First, the acid content of the crude NC is reduced to a low (0.25-0.50 percent) level by water washing. Then, the NC receives several boiling treatments to destroy unstable sulfate esters and nitrates of partially oxidized cellulose by acid hydrolysis. Next, the product is beaten in a Jordan beater to reduce the NC fiber length and remove traces of occluded acid. Finally, the NC is boiled in dilute sodium carbonate solution, then washed with water until free of alkali. After purification, the NC is centrifuged to approximately 30 percent moisture, and then processed in accordance with the specific end-use requirements of the batch. Nitrocellulose is a principal ingredient of most propellants (single-base; combined with nitroglycerin in double-base propellants; combined with nitroglycerin and nitroguanidine in triple-base propellants). NC is used in smokeless powder, rocket grains, ball powder and mortar increments, as well as some explosives (2b).

d. In the continuous process, linters are continually nitrated and dumped to a centrifuge to recover acid. The crude NC is washed, recentrifuged, slurried in water and boiled. The remaining steps are as described above for the batch NC process.

38. Waste Sources

a. In the manufacture of nitrocellulose, repeated washing yields wastes with varying acid content, from highly concentrated acidic effluents to alkaline ones, some having an elevated temperature. Volumes of wastewater generated, per lb of NC produced, have been variously reported as a lowest value of 16 gal/lb (2b) up to a high value of 100 gal/lb (16zt). Figure 9 is a schematic of current water use at Radford AAP.

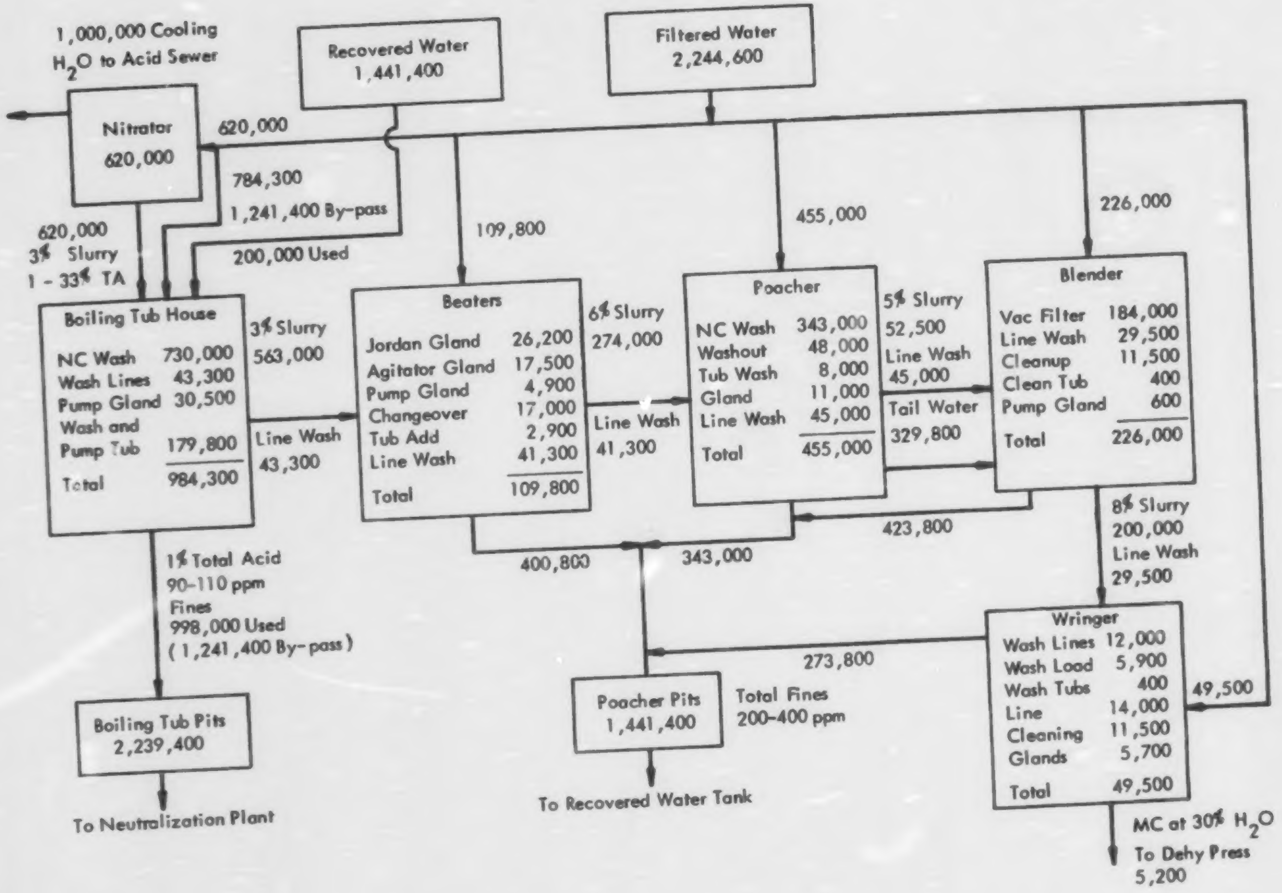
1,000,000 Cooling
H_2O to Acid Sewer
Recovered Water
1,441,400
Filtered Water
2,244,600
Nitrator
620,000
620,000
784,300
1,241,400 By-pass
200,000 Used
620,000
3% Slurry
1 - 33% TA
109,800
455,000
226,000
Boiling Tub House
NC Wash 730,000
Wash Lines 43,300
Pump Gland 30,500
Wash and Pump Tub 179,800
Total 984,300
3% Slurry
563,000
Line Wash
43,300
Beaters
Jordan Gland 26,200
Agitator Gland 17,500
Pump Gland 4,900
Changeover 17,000
Tub Add 2,900
Line Wash 41,300
Total 109,800
6% Slurry
274,000
Line Wash
41,300
Poacher
NC Wash 343,000
Washout 48,000
Tub Wash 8,000
Gland 11,000
Line Wash 45,000
Total 455,000
5% Slurry
52,500
Line Wash
45,000
Tail Water
329,800
Blender
Vac Filter 184,000
Line Wash 29,500
Cleanup 11,500
Clean Tub 400
Pump Gland 600
Total 226,000
423,800
400,800
343,000
8% Slurry
200,000
Line Wash
29,500
1% Total Acid
90-110 ppm
Fines
998,000 Used
(1,241,400 By-pass)
273,800
Wringer
Wash Lines 12,000
Wash Load 5,900
Wash Tubs 400
Line 14,000
Cleaning 11,500
Glands 5,700
Total 49,500
49,500
Boiling Tub Pits
2,239,400
To Neutralization Plant
Poacher Pits
1,441,400
Total Fines
200-400 ppm
To Recovered Water Tank
MC at 30% H_2O
To Dehy Press
5,200

Figure 9 - Current NC Water Use (gpd) at Radford AAP - One Line NC Capacity; 144,000 lb/day (Pulp), or 120,000 lb/day (Linters) (3u)

Wastewater volumes for that facility are summarized in Table 19. Of the total, 29.1 percent is cooling water used only during the summer months. The boiling tub operations use 200,000 gpd of recycled wastewater from the combined discharge of the last four sources shown in Table 19. Excluding cooling water, the process water use for the flows presented in Table 19 is 16.9-20.3 gal/lb NC. Approximately 45,000 gpd of this water is used to transport the NC from process to process, as a 3-10 percent solids slurry. The wastewater discharge from total NC production at Radford AAP is reported to be about 10 MGD (15zp).

b. Modernization of the NC process at Radford AAP will result in a continuous cellulose nitration process. As presently designed (Figure 10), the continuous process will use 432,000 gpd recycle cooling water (summer only) versus 1 MGD for the batch process, and 441,880 gpd recycle wastewater for the boiling tubs versus 998,000 gpd with the present batch system. The boiling tub water will be recycled to an acid content which will permit economical acid recovery (15zp). Water needed for the remaining operations of the continuous process will be identical to the present system, but will be used counter current to process flow, with ultimate disposal to the NAC acid recovery process (15zp). In addition, the finished NC will be transported by slurry (150,000-160,000 gpd) to modernized continuous automated single- and double-base propellant lines (3u).

c. As shown on Figure 9, the batch process wastewaters contain considerable amounts of acid and suspended solids. A discharge of 0.7-1.0 lb sulfuric acid/lb NC, and 0.3-0.4 lb nitric acid/lb NC, has been reported (2b). The suspended solids are essentially fine particles of NC. A typical size distribution of these NC fines is presented in Figure 11. Fifty percent of the particles are less than 2 microns in size. There is no NC in solution, since NC is essentially insoluble in water (2b). In addition to NC fines and nitrating acids, present wastewaters contain alkali from neutralization steps, and soluble organic compounds such as esters of oxy-cellulose (16zt).

d. Good wastewater characterization data are available from Radford AAP (1n3). Selected parameters of the waste discharge for each NC processing step are summarized in Table 20. For each source described in Table 20, there are normally several sequential processing steps, such as fill and drain rinses. The wastewater generally becomes more dilute with each sequential step, so that the range of data reported in Table 20 spans the first, most concentrated rinse to the last, most dilute rinse. For example, sequential samples taken at Boiling Tub House #1019 showed pH values of 1.4, 1.6, 3.1 and 3.2. On the basis of waste characteristics, the Boiling Tub House effluent is much different than other sources, being very acidic and high in nitrate, but low in suspended solids. The other process effluents are more nearly neutral and low in nitrate, but high in suspended solids as a result of the NC fines discharged.

e. The Boiling Tub wastes at Badger AAP are also characterized by low pH (range 0.4-3.3, average 1.4), high nitrates (range 100-

Table 19. Wastewater Volumes from NC Production at Radford AAP (3u)

Source	Volume*, gpd	Percent Use
Nitration Cooling	1,000,000	29.1
Boiling Tubs	998,000	29.0
Beaters	400,800	11.7
Poachers	343,000	10.0
Blenders	423,000	12.1
Wringer	273,800	8.0
TOTAL	3,438,600	100.0

*Flow per NC line. NC capacity per line is 120,000-144,000 lbs/day.

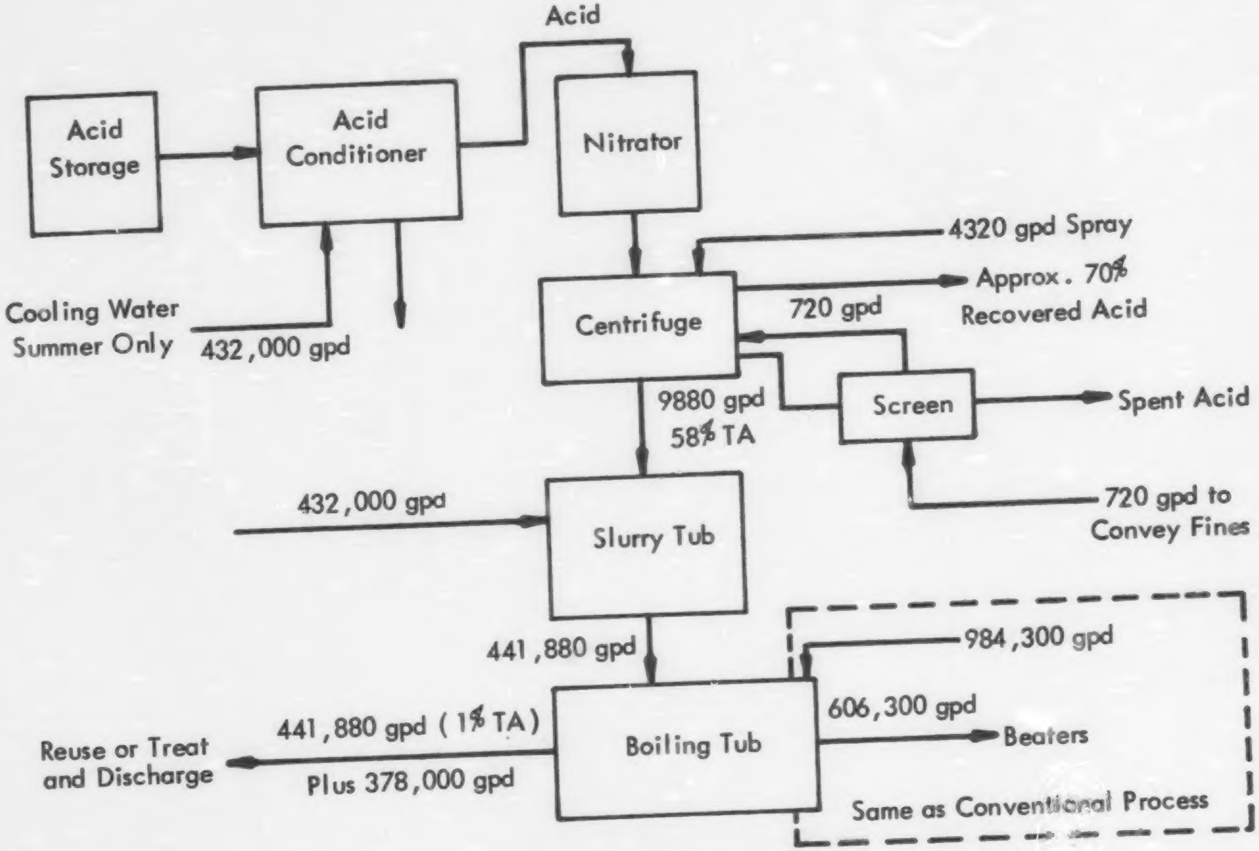
Acid
Acid Storage
Acid Conditioner
Nitrator
Cooling Water Summer Only
432,000 gpd
4320 gpd Spray
Centrifuge
720 gpd
Approx. 70% Recovered Acid
9880 gpd 58% TA
Screen
Spent Acid
720 gpd to Convey Fines
432,000 gpd
Slurry Tub
441,880 gpd
984,300 gpd
606,300 gpd
Beaters
Boiling Tub
441,880 gpd (1% TA)
Plus 378,000 gpd
Reuse or Treat and Discharge
Same as Conventional Process

Figure 10 - Water Balance for Continuous NC Line (3u)

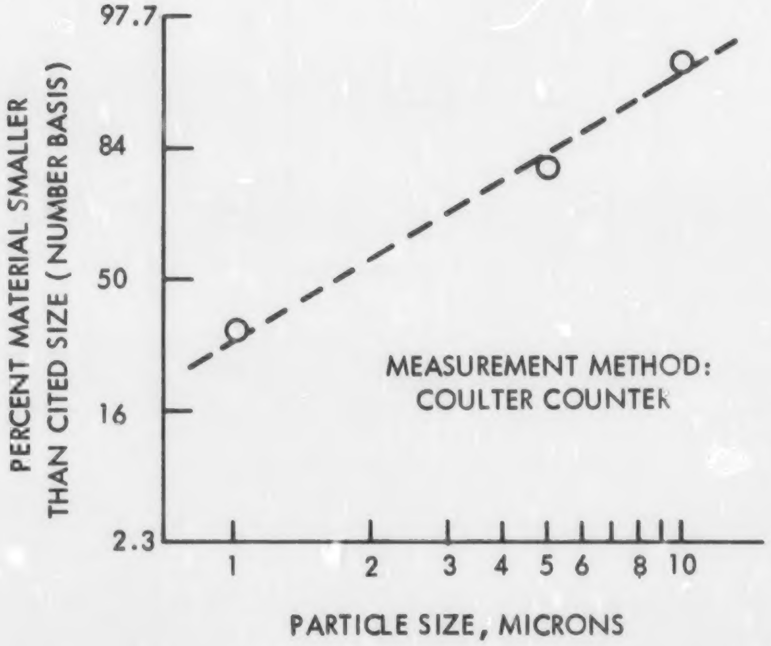

Figure 11 - Boiling Tub Pit Water Nitrocellulose Fines (2b)

Table 20. Wastewater Characteristics of Radford AAP NC Processes (ln(3))

Source	pH	Suspended Solids, mg/1		Filtered COD, mg/1		Nitrate+Nitrite-N, mg/1	
		Range	Average	Range	Average	Range	Average
Boiling Tub Houses							
#1019	1.4-3.2	1-22.0	8.30	32-270	103.5	7.1-1000	406.8
#2019	1.1-3.9	1-62.5	10.0	105-152	136.0	9.0-1000	277.3
Jordan Beater Houses							
#1022	7.2	-	140	-	-	-	-
#2022	7.6-9.1	290-1054	580	-	31.0	0.6-4.0	2.2
Poacher-Blender Houses							
#1024 (Poach)	6.6-9.8	52.0-632.0	278.9	-	-	1.0-60.0	21.1
#2024 (Poach)	5.5-9.0	23.0-526.0	214.1	72-685	414	100-70.0	26.9
#1024 (Blend)	6.0	463-495	479.0	-	-	30.0-34.0	32.0
Wringer House	7.4-8.2	343-828	518	-	135	-	-

1350 mg/l, average 700 mg/l) and sulfate (range 75-5100 mg/l, average 2600 mg/l). The waste is thus similar to Radford AAP, and although sulfate data for Radford are not available, they are likely equivalent to the Badger wastewater. Composite wastewater suspended solids concentration for the Badger NC line is 43 mg/l (2b).

39. Effects of Water Management

a. There is significant opportunity for reduction in wastewater volume, and mass pollutant discharge, by water management. Use of a cooling tower and recycle system will reduce water discharged at Radford AAP during the summer by 1 MGD (3h). The two basic pollutants resulting from NC manufacture are nitrating acids and NC fines. Figure 12 shows a proposed recycle water management program, which would reduce process wastewater discharge by 90-95% (16j). The program involves recycle of boiling tub water through the nitrator, up to a total acid content of 13 percent. With a 13 percent maximum acid level, this flume line water can be cycled up to six times, and then discharged to the NAC acid recovery plant for recovery of nitric and sulfuric acids (3u). Implementation of recycle and acid recovery will save about $10 million in capital investment for denitrification facilities at Radford AAP (15zp).

b. For the more neutral, but suspended solids-laden wastewater from the remaining batch processes, centrifugation treatment allows both recovery of NC fines and recycle of the water. Fines collected by centrifugation will be blended into the NC process, where practical, with the remainder of the fines being disposed as solid explosive wastes (3u). One problem encountered in the reuse of water in the NC purification process is the buildup of sodium nitrate and sodium sulfate, resulting from neutralization of acids with sodium carbonate. The buildup of these salts will be only about 27 mg/l per cycle for the conventional batch line and 9 mg/l for the continuous line (3u). This may necessitate blowdown from the recycle system, and Radford AAP has proposed a blowdown flow of 200,000 gpd (6a). If blowdown could be avoided, the NC process could be totally closed, with complete wastewater recycle plus recovery of NC and acids.

c. A similar recirculating system has been suggested for the continuous NC process, with recycle of Boiling Tub water to achieve 15-20 percent acid levels, and centrifugation for NC fines control (3u).

40. Current Treatment Practice

a. At both Badger and Radford AAP's, spent nitrating acid is separated from the crude NC and processed for acid recovery. At Radford AAP, acid wastewater generated from washing the NC after each process step in the Boiling Tub House is diverted to settling pits, for partial removal of NC fines. The more neutral wastes from the Jordan Beater House, Poacher-Blender House and final wringer house go to a separate set of settling pits. Average NC fines concentration for the Boiling Tub discharge is less than 10 mg/l, and ranges from 104-580 mg/l for the

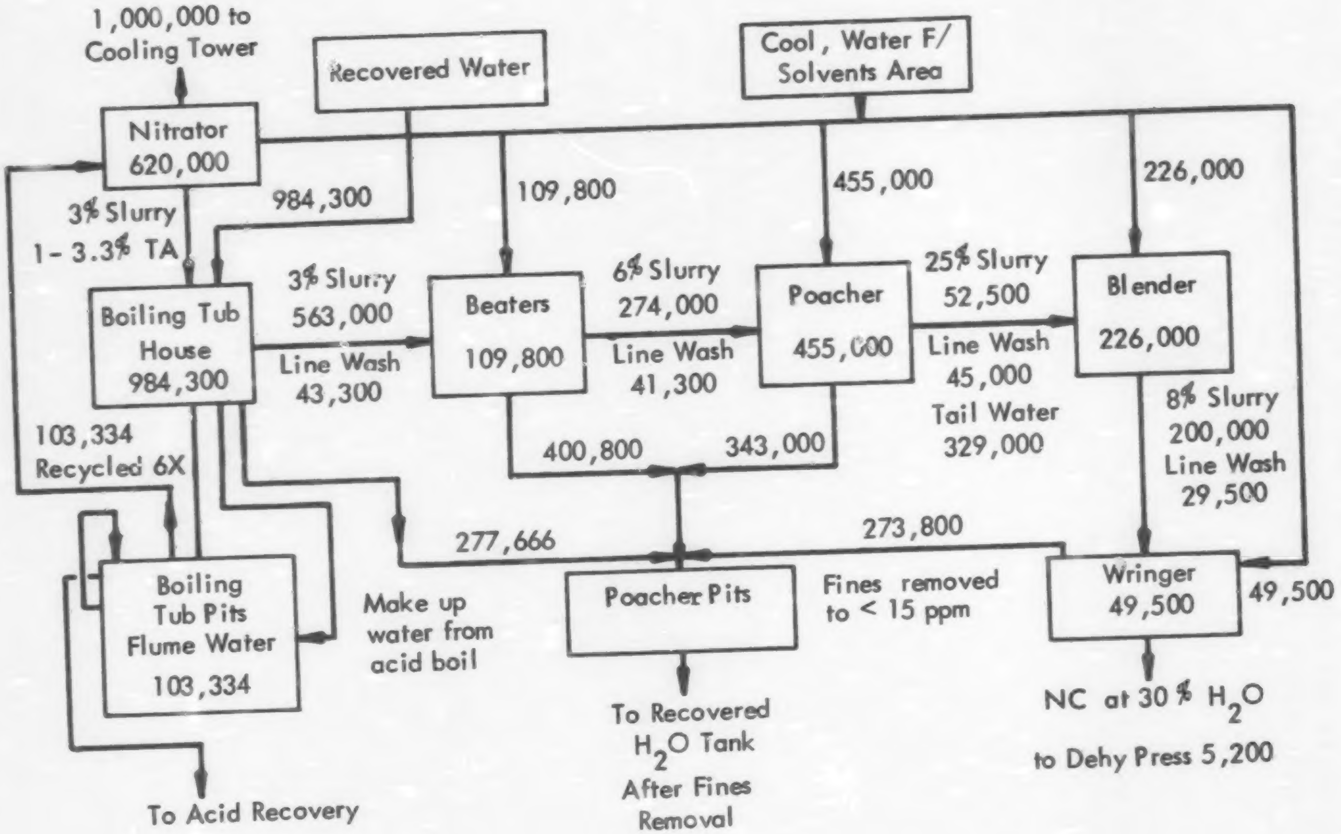
1,000,000 to Cooling Tower
Recovered Water
Cool, Water F/ Solvents Area
Nitrator 620,000
984,300
109,800
455,000
226,000
3% Slurry
1- 3.3% TA
Boiling Tub House 984,300
3% Slurry 563,000
Line Wash 43,300
Beaters 109,800
6% Slurry 274,000
Line Wash 41,300
Poacher 455,000
25% Slurry 52,500
Line Wash 45,000
Tail Water 329,000
Blender 226,000
8% Slurry 200,000
Line Wash 29,500
103,334 Recycled 6X
400,800
343,000
277,666
273,800
Boiling Tub Pits Flume Water 103,334
Make up water from acid boil
Poacher Pits
Fines removed to < 15 ppm
Wringer 49,500
49,500
To Recovered H_2O Tank After Fines Removal
NC at 30 % H_2O
to Dehy Press 5,200
To Acid Recovery

Figure 12 - Proposed NC Water Balance (6a)

other processes (Table 20). No information is available on the efficiency of fines removal in the settling pits, but the small size of the fines (Figure 11) suggests that significant quantities of fines overflow the settling pits.

b. The pit effluent is currently treated, along with acid area wastewater, with lime in a neutralization plant. The neutralization facility consists of two baffled lagoons operated in parallel, preceded by a slaked lime slurry feeder. The influent is heavily diluted with cooling water (4c). The plant is reported to perform inadequately, with fluctuations in pH, and high effluent levels of solids, nitrate, sulfate and COD (4c). Sulfate control would be enhanced through calcium sulfate precipitation, if process wastewater were treated prior to dilution with cooling water. Influent and effluent characteristics are presented in Table 21. Effluent suspended solids are 535 mg/l (average), representing a removal efficiency of only 44 percent.

c. Badger AAP also uses settling pits for roughing treatment of NC wastewaters. Overflow for the Boiling Tub Houses settling pits flows to a waste acid neutralization facility, where lime slurry is added. Control of pH is automated, with a feedback pH controller (3f). The system does not function adequately, with effluent pH values of 1.7-12.2 reported for influent pH of 0.4-3.2 (1a(3)). The effluent also contains high levels of nitrate (434 mg/l), sulfate (1605 mg/l), and suspended solids (287 mg/l). Influent suspended solids to the Badger AAP neutralization facility averaged only 6.1 mg/l (1a(3)). The high effluent value likely reflects discharge of precipitates yielded in the neutralization reactions.

d. The neutralization plant at Badger AAP receives only Boiling Tub House settling pit overflow. Wastewater from other NC processing houses, after settling pit treatment, is either discharged without further treatment or recycled for use in NC slurry transport lines (3f). This wastewater is reported to have the following characteristics: pH, 1.5-6.9; nitrate - N, 7.1-31.8 mg/l; sulfate, 63-195 mg/l; COD, 64-112 mg/l; and suspended solids (NC fines) 63.5-138 mg/l (1a(3)).

e. Thus, on the basis of the above information, there is essentially no effective treatment applied to wastewaters of NC manufacture. Treatment is limited to partial removal of suspended solids by settling pits, and some rather ineffective efforts to adjust pH, with the exception that there is no pH treatment at all for Badger AAP wastewaters other than from the Boiling Tub Houses.

41. Modifications to Current Treatment

a. Both Badger and Radford AAP's have approval for, and are implementing changes in current waste treatment practice. Modifications related to control of NC fines will be tested at Radford, with successful technology transferred to Badger AAP. Both plants have on-going programs to improve treatment of acidic wastewaters.

Table 21. Performance Data on Radford AAP Facility for NC and Acid Area Wastes (ln(2))

Parameter	Ave. Concentration, mg/l*		Percent Removal
	Influent	Effluent	
pH	6.3	6.4	-
Total Solids	3563	3397	4.7
Volatile Solids	396	376	5.0
Suspended Solids	956	535	44.0
Settleable Solids	0.24	0.07	70.8
Nitrate-N	271.9	299.8	+10.3
Sulfate	1199	1208	+ 0.7
COD	-	80	-

*Except pH.

b. At Badger AAP, a new industrial wastewater treatment facility is under construction. The facility will provide equalization, mixing, aeration, and neutralization through chemical addition (1a)2)). This facility will treat all industrial wastewater concurrently discharged through the Badger main plant outfall. This includes wastewaters from the nitric acid plant, NC production and solvent recovery. The new facility should be effective in pH control, but does not incorporate processes for BOD, nitrate, sulfate or effective suspended solids removal. A second treatment plant is thus under construction to treat the effluent from the waste acid neutralization facility (3f). This second facility is intended to provide reduction of BOD and solids. Depending upon the solids separation technology utilized, this second plant should achieve effective BOD and suspended solids control, although nitrate and sulfate will be unabated.

c. At Radford AAP, two modifications to current treatment are undergoing implementation. One modification is for NC fines and the second for acidic wastewaters. Installation of centrifuge units is planned for NC fines control (6a). Centrifugation would follow the settling pits. In prototype centrifuge tests at Radford, a DeLaval unit operating at 5,500-9,000 gph reduced NC fines in Boiling Tub pit effluent (188 mg/1), poacher pit (477 mg/1) and tail water (230 mg/1), to below 25 mg/1) (6a). Average flow was 8,000 gph. Centrifugation is claimed to have the following advantages (6a):

(1) no additives are required (which would contaminate the recovered NC)

(2) direct return of NC fines for reuse

(3) reuse of the clarified effluent.

Current plans are to install a 10,000 gph centrifuge, on a trial basis, at Radford AAP by 1976 (4c).

d. In addition, improved neutralization facilities, similar to those to be installed at Badger, are planned for Radford AAP. Modifications to the present neutralization lagoons will include equalization tanks, additional tanks for improved mixing and longer retention times for pH control, settling tanks with flocculation capability for improved removal of the settleable solids, and mechanical sludge removal and sludge dewatering (6a). Since the major shortcoming of present neutralization facilities at both Radford and Badger is lack of adequate reaction time, compounded by feedback automatic lime addition, the use of flow equalization, together with better mixing and longer reaction tank retention times, should provide improved neutralization. As at Badger AAP however, the proposed Radford treatment plant has no provision for control of BOD, nitrate or sulfate.

42. Alternatives to Current Practice

a. The single unique constituent of wastewaters from nitrocellulose manufacture is NC fines. Other wastewater parameters include acidic to near-neutral pH, sulfate, nitrate and moderate to high COD. These latter waste constituents are typical of acid manufacturing wastes, and pH, nitrate and sulfate may be controlled by the technology discussed in Section III of this chapter.

b. The biodegradability of the COD constituent of the wastewaters is unknown. Measured soluble COD's ranged up to 414 mg/l at Radford AAP (Table 20). This likely represents soluble organic compounds such as esters of oxycellulose (16zt). NC itself is essentially insoluble, and not readily biodegraded (2b). Thus, the soluble organics of NC wastewater presumably consist of incomplete reaction products, plus products of alkaline neutralization and other NC cleaning processes. In biodegradation studies on caustic-digested NC fines, an activated sludge process (bench-scale) reduced BOD and COD from 240 and 724.5 mg/l to 27.3 and 324.2 mg/l, respectively (3h). Thus, although good BOD removal was shown (88.6%), a large fraction of the COD and TOC (about 45%) was not removed by biological treatment. It is probable that the same situation would hold for the NC manufacture wastes, with effective removal of the BOD fraction by biological treatment, but high effluent COD levels.

c. The insolubility of NC, and its presence in wastewater as fine suspended solids, indicates that any of several solids removal technologies, such as centrifugation, coagulation and/or filtration, could be employed. Centrifugation has been pilot tested at Radford AAP, achieving suspended solids reduction to less than 25 mg/l (6a). Other solids removal processes include dissolved air flotation, coagulation-flocculation, granular filtration and resonating filters. Dissolved air flotation was unsuccessful when tested at Radford AAP (6a). Undoubtedly coagulation and flocculation would be effective on NC fines, and is a proven process for similar applications of suspended solids removal. However, the process is expensive when compared to other alternatives and additionally results in a sludge from which NC could not be recovered. In granular filtration tests at Radford, Boiling Tub pit effluent was reduced to below 15 mg/l suspended solids, but granular filtration of poacher pit effluent resulted in suspended solids levels exceeding 40 mg/l (6a). By comparison with centrifugation, granular filtration is thus less effective.

d. A newly developed micropore filtration process has proven successful in pilot treatability studies on pulp and paper mill wastewaters. The patented "Hydroperm" system (HYDRONAUTICS, Inc.) has achieved 88 to 100 percent removal of suspended solids at a filration pressure of 15 psi (16zv). Particle characteristics of the pulp and paper mill wastes should be similar to NC fines. However, approximately 30 percent of NC fines are less than one micron in size (Figure 11), and no information is available on the minimum size of effective particle removal by the micropore filtration process.

e. Tests at Radford in NC fines removal with a resonance filter were inconclusive. Difficulties included a too fragile filter medium, with too large pore size to remove the finer fraction of suspended solids (6a). Thus, among the available proved processes, coagulation and centrifugation are most effective, with centrifugation having the advantage of NC recovery. In summary, the current Army program for pH control and NC fines abatement appears to be drawn from best available technology. When coupled with available water management techniques, and sulfate and nitrate abatement procedures, the wastewater resulting from NC manufacture can be totally controlled.

43. Summary

Although wastewaters from NC manufacture are not currently receiving adequate treatment, beyond partial pH adjustment, at either Badger or Radford AAP's, major efforts have been initiated at both plants for improved pollution abatement. The program at Radford AAP in water conservation and reuse plus recovery of NC and acids, is particularly notable. Current plans call for essentially complete recycle and recovery, with the exception of some blow-down from the acid neutralization wash. Although Badger AAP also will incorporate some new treatment procedures, they are essentially limited to pH, solids and BOD control. A more rigorous abatement effort is indicated for Badger AAP, encompassing both recycle and recovery, plus nitrate and sulfate control.

SECTION V - RDX AND HMX

44. Introduction

a. RDX (cyclotrimethylenetrinitramine) is a major military explosive, used as a component in many explosive and propellant formulations. HMX (cyclotetramethylenetetranitramine) is a by-product of RDX manufacture, and is also used as a component of explosive formulations as well as solid missile propellants. Mixtures of RDX and wax, called "Composition-A" explosives, are used in artillery shells. Compositions A-3 and A-5 are also used as booster charges in many Army munitions, in lieu of tetryl. Mixtures of RDX or HMX with special plasticizers and solvents give rise to numerous plastic explosives and demolition charges such as "Composition-C," or "PBX" explosives. RDX and HMX find wide application in bomb and artillery shells. For this purpose they are mixed with TNT to form mixtures called "Composition-B," "cyclotols" or "octols." RDX and HMX, and the various explosive formulations derived from them, are produced only at Holston AAP. However the composition explosives which incorporate RDX and HMX are loaded at several Army and Navy LAP plants, and LAP air scrubber and clean-up waters thus contain these explosives as contaminants.

b. RDX and HMX are manufactured by the same processing stages, using the same ingredients. The two different products result from using different proportions of reactants. The reactants for RDX and HMX, for a hypothetical 100 lb reactant charge, are presented in Table 22.

c. In RDX manufacture, the ingredients are charged to a reactor at 75°C. The initial crude product contains about 79% RDX, 6% HMX and various intermediate products. The reaction mixture goes through an aging and simmering process to convert these intermediates to RDX or decompose them. HMX is not considered detrimental to RDX performance, and no attempt is made to separate or recover it (2c).

d. The reaction mixture is cooled, and most of the crude RDX crystallizes and precipitates. Most of the supernatant liquor is drawn off by vacuum and transferred to a recovery building. The processing of this supernatant was described in Section III of this chapter. After vacuum filtering, the crude RDX is washed with water. The wash water is withdrawn by vacuum and recycled to the simmering process (Figure 7, Section III). The RDX is then slurried in additional water and transferred to a recrystallization process. There, cyclohexanone is added to the slurry, the slurry heated, and the cyclohexanone distilled, with RDX recrystallizing in particles of acceptable size. The RDX in water slurry is then poured into special vacuum carts (nutsches) and most of the water withdrawn. The resulting explosive contains about 10% residual moisture (2c). When RDX is heated and mixed with wax, TNT or other ingredients of composition explosives, this residual water separates and is decanted as a wastewater. The major incorporation product is Composition B, which contains 60.5% RDX, 38.7% TNT and 0.8% wax. Incorporation water will contain TNT in addition to RDX.

Table 22. Reactants for RDX and HMX Manufacture (2c)

Reactant	RDX, lbs	HMX, lbs
Ammonium Nitrate	17.2	11.0
98% Nitric Acid	13.6	
Hexamethylenetetramine	9.2	17.0
Acetic Acid	15.0	18.0
Acetic Anhydride	45.0	54.0

e. For HMX manufacture, the same production steps are employed. About 27% of the crude product is RDX. Most of the RDX is extracted in the acid draw-off by vacuum and washing steps, and eventually is added to RDX production. The HMX recrystallization process is usually accomplished with acetone, rather than cyclohexanone. The major wastewater discharges for HMX production occur during the dewatering steps, and during incorporation into composition explosives such as Octol.

f. RDX and HMX solubilities will influence their concentrations in wastewater, which may also contain acetic anhydride, cyclohexanone (for RDX) or acetone (for HMX). Selected solubilities are presented in Table 23. As is indicated by those data, both RDX and HMX are extremely soluble both in warm water and organic solvents.

g. At many LAP facilities, shells and bombs are filled with explosives which incorporate RDX or HMX. Typically, the composition explosive is ground or otherwise broken up, melted and poured into shells and bombs. RDX and HMX-contaminated wastewaters from these LAP operations include fume and dust control scrubber water, and washwater from spills and floor and equipment washdown. Similar wastewaters may also result from explosive steamout from rejected shells (2c).

45. Waste Sources

a. The major wastewater sources from RDX and HMX manufacture result from dewatering of the explosives in nutsches, decanting water from hot composition explosive blending, and floor and equipment cleanup. In addition, explosives contaminated wastewater results from dust control by scrubbers at the Holston AAP explosives packaging buildings. Most discharges flow through catch basins, to provide removal of settleable solids, before wastewater discharge.

b. Pollutant discharge data are presented in Table 24 for RDX manufacture,, and Table 25 for HMX manufacture. The wastewater discharge resulting from explosives packaging (Table 24, Building N-7) results from air pollution scrubber operation. Greatest wastewater volumes from production are associated with the nitration process and nutsch dewatering, with an additional high flow from incorporation. Highest concentration of explosives results from nutsch dewatering, the incorporation step and scrubber operation in explosives packaging. These latter two sources also contain significant TNT levels. All catch basin effluents discharge to an industrial sewer and thence to the Holston River, without additional treatment. It has been reported that Holston AAP discharges 920-1200 lbs/day of RDX, and lesser amounts of HMX and TNT to the river (4b).

c. Table 26 presents flow data, from a 1971 study, of process-contaminated waste volumes and non-contact discharge volumes. Non-contact water includes heat exchange cooling, steam condensate and pump seal water. Differences in flow volume between Table 26, and Tables 24 and 25, likely reflect changes in daily explosives production rates. Contaminated process water for most of the manufacturing buildings represents only a small fraction of the total discharge to the catch basins.

Table 23. Selected Solubilities of RDX and HMX (2c)

Solvent	RDX Solubility	HMX Solubility
Water @ 25°C	7.6 mg/1	-
Water @ 83°C	1.3 g/1	0.14 g/1
Acetone @ 30°C	69.0 g/1	22.0 g/1
Cyclohexanone @ 30°C	84.0 g/1	53.0 g/1
Acetic Anhydride @ 30°C	49.0 g/1	13.0 g/1

Table 24. Pollutant Discharge from RDX Manufacture at Holston AAP (5d, 5e)

Production Source	Catch Basin Influent (I) or Effluent (E)	Wastewater Volume, gpd	Concentration, mg/1			
			BOD	RDX	HMX	TNT
Nitration Reactor (D-2*)	I	49,760	2359	5.06	2.17	-
	E	49,760	2116	2.31	0.96	-
Filtration and Washing (E-3*)	I	13,856	582	4.15	1.87	-
	E	13,856	1163	3.53	0.00	-
Recrystallization (G-2*)	I	27,218	896	0.0	0.0	-
	E	27,218	339	0.0	0.0	-
Nutsch Dewatering (H-2*)	I	346,523	2771	49	1.5	-
	E	346,523	3229	33	0.7	-
Incorporation-Composition B (J-2*)	I	118,803	5895	13.12	0.10	24.2
	E	118,803	4500	11.10	0.06	12.1
Explosives Packaging (N-7*)	I	742	3747	13.0	14.0	237
	E	742	3151	6.0	8.0	129

*Indicates Holston AAP Building for which data reported.

Table 25. Pollutant Discharge from HMX Manufacture at Holston AAP (5e)

Production Source	Catch Basin Influent (I) or Effluent (E)	Wastewater Volume, gpd	Concentration, mg/l		
			BOD	RDX	HMX
Nitration Reactor (D-6*)	I	18,800	2393	0.0	0.0
	E	18,800	1840	0.0	0.0
Filtration and Washing (E-6*)	I	-	5183	70.1	45.7
	E	-	6098	6.1	12.2
Recrystallization (G-6*)	I	135,807	331	5.2	10.6
	E	135,807	322	5.2	4.4
Nutsch Dewatering (H-6*)	I	-	394	21.5	34.5
	E	-	375	20.9	9.2

*Indicates Holston AAP Building for which data reported.

Table 26. Discharges to Catch Basins at Holston AAP (1d(2))

Building	Product	Process Wastewater, gpd	Non-Contact Water, gpd	Total Flow, gpd	Percent Process Wastewater
D-6	HMX	2,500	38,710	41,210	6.1
D-8	RDX	2,900	39,420	42,320	6.8
E-8	RDX	1,640	6,480	8,120	20.2
G-8	RDX	1,440	5,420	6,860	20.9
G-4	RDX	77,740	39,540	117,280	66.1
H-6	HMX	10,740	12,500	23,240	46.2
H-8	RDX	54,480	2,880	57,360	94.8

D - Buildings are Nitration Reactors
E - Buildings are Filtration and Washing Operations
G - Buildings are Recrystallization Processes
H - Buildings contain Nutsch dewatering equipment

d. Limited information is available on wastewater characteristics associated with handling and loading of RDX and HMX based explosives at LAP facilities. Available data are tabulated in Table 27. Wastewaters from melt-pour operations result from condensed steam and washwater, primarily. Bomb Plant A at NAD Crane (Table 27) also includes a demilitarization facility. Bomb Plant B was not in operation at the time of preparation of this report. Other plants also handle RDX and HMX, and have associated wastewaters. For example, NAVPRO Magna grinds HMX-based explosives, and uses catch basins for partial wastewater treatment. No explosive concentration data are available, however (15zj). Evidence of groundwater contamination by RDX has been reported at NAD Crane (14y). Water samples taken from on-station monitoring wells have been found to contain 0.0 to 7.9 mg/l RDX, with nearby streams containing RDX at 3.0-10.0 mg/l. Most wells sampled were shallow, and there appears to be a strong correlation between stream water and well water RDX content. TNT, monitored concurrently with RDX, was much lower in both streams and wells (14y). In addition, RDX levels showed rapid attenuation at greater distances away from streams. Over a distance of 28 ft from one well, RDX was reduced from 4.1 to 0.24 mg/l (14y).

46. Effects of Water Management

a. The most notable effort in water management associated with RDX and HMX manufacture is the return of the first wash water after nitration to the nitration process. This wash water, which is acidic and high in nitrate, ammonia, acetate, explosives products and reaction intermediates, would otherwise represent a major pollutional source. One of the five Composition B lines at Holston AAP is to undergo modernization. This modernized line will incorporate several water management techniques to eliminate pollutant discharge. These will include: elimination of the decantation water resulting from melting of RDX, recycle of spray water used to cool molten Composition B, and recycle of fume scrubber water, after carbon treatment. Wastewater from the remaining four Composition B lines, which will not undergo modernization, will be handled by wastewater treatment processes described in paragraph 48.

b. Based upon the data of Table 26, it appears that the segregation of non-contact from process cooling water offers a significant opportunity for water management and reduction in contaminated wastewater volume. Discharge for the "D" Buildings to the catch basins contains less than 7 percent process effluent, while discharge from all except Buildings G-4 and H-8 represent less than 50 percent process effluent. Segregation of non-contaminated discharges would provide greater detention time in the catch basins, and result in smaller wastewater volumes for additional treatment.

c. Aside from the possibility of dry rather than wet dust control systems, discussed in paragraph 50, other opportunities for effective water management are limited.

Table 27. RDX and HMX Wastewaters Resulting from LAP Activities

LAP Facility	Activity	Volume, gpd	Concentration, mg/l		Treatment	Reference
			RDX	HMX		
Joliet AAP	Melt-Pour LAP Laundry	6,200 9,600*	87-180 1.1		Activated Carbon None	8f 8f
Milan AAP	Melt-Pour	-	1.1-2.2		Catch Basin & Evap. Pond	31
Iowa AAP	Melt-Pour	-	18-24		-	13e
NAD Crane	Air Scrubber and Melt-Pour (Rockeye Plant)	-	0.0	1.0-16.0	Catch Basin	14f
	Melt-Pour (Bomb Plant A)	-	17.9	0.0-0.9	Catch Basin	14f
	Melt-Pour (Bomb Plant B)	-	12.8-41.6	0.0-5.5	Catch Basin	14f

*20 gpm, based on 8-hour operation.

47. Current Treatment Practice

a. With the exception of activated carbon treatment of LAP wastewater at Joliet AAP, and some limited application of solar evaporation ponds to wastewaters at other LAP facilities, treatment of RDX and HMX wastewater from both manufacture and LAP is limited to catch basins or baffled sumps. These devices are intended to remove only the larger settleable solids and, if subjected to hydraulic overload, will have very low efficiency of removal even for that constituent of the wastewater. Based upon the data of Table 24, the efficiency of RDX removal at Holston AAP ranges from 0.0 to 91.3 percent, with an average removal efficiency of 33.2 percent. Effluent RDX concentrations range from 0.0-33 mg/l, as shown in Tables 24 and 25. The efficiency of HMX removal at Holston AAP ranges from 40-100 percent, averaging 62.1 percent removal efficiency. This higher removal may reflect the lower solubility of HMX.

b. Both Milan AAP and NAVPRO Magna use catch basins, followed by solar evaporation ponds, for LAP wastewaters. In neither case is there a surface discharge from the ponds. However, the use of evaporation ponds depends upon proper climatological conditions, and facilities located in geographical regions which do not provide these conditions must utilize alternate treatment methods.

c. Joliet AAP treats one Composition B LAP wastewater stream by a combination diatomaceous earth filtration and activated carbon adsorption process. The process uses two carbon columns, connected in series and piped so that the columns may be used in either order. Because the carbon cannot be effectively regenerated, the carbon in the No. 1 column is replaced monthly (1g(3)). Spent carbon and backwashed solids from the filter are burned. Wastewater is pumped through the system at a fairly constant rate of 12-15 gpm. Operating on an eight-hour shift, the treated wastewater volume is about 6200 gpd. Table 28 presents operating data for the system. Although removal efficiency is good for suspended solids and TNT, RDX removal is less efficient, with an average effluent RDX level of 19 mg/l, and maximum of 46 mg/l. Further, most removal occurs in the first carbon column, as shown in Table 29. The diatomaceous earth filter provides essentially no removal, and the second carbon column very little additional removal after the first.

d. While activated carbon is effective in removing TNT from wastewater, its efficiency is significantly less for RDX, as shown in Figure 13. It has been reported that activated carbon adsorptivity of RDX is only about 16-17 percent of carbon adsorptivity for TNT (15zk). This indicates that in a mixed RDX plus TNT wastewater, only a fraction of the TNT capacity will have been exhausted prior to RDX breakthrough. Further, it has been reported that TNT will displace and leach adsorbed RDX from a carbon column (14z). This does not imply that activated carbon cannot be used for RDX removal and, in fact Yorktown Naval Weapons

Table 28. Performance of Joliet AAP Treatment System (1g(3))

Parameter*	Influent		Effluent		Average Percent Removal
	Range	Average	Range	Average	
pH	6.8-8.4	7.9	6.7-8.0	7.7	-
Total Solids	903-1790	1401	762-1497	1070	23.6
Suspended Solids	22-336	138	0-7	1.2	99.1
TNT	156-235	178	0-25	3.7	97.9
RDX	87-180	145	0-46	19	86.6

*Concentration in mg/l, except pH.

Table 29. Performance of Individual Units of Joliet AAP Treatment System (lg(3))

Treatment Unit	Suspended Solids		TNT		RDX	
	Concentration, mg/l	Cumulative Percent Removal	Concentration, mg/l	Cumulative Percent Removal	Concentration, mg/l	Cumulative Percent Removal
Raw Waste	138.5	-	178.2	-	145.2	-
Filter	108.6	21.6	175.7	1.4	148.9	(-2.5)
1st Column	8.4	93.9	14.7	91.8	30.1	79.3
2nd Column	1.2	99.1	3.7	97.9	19.5	86.6

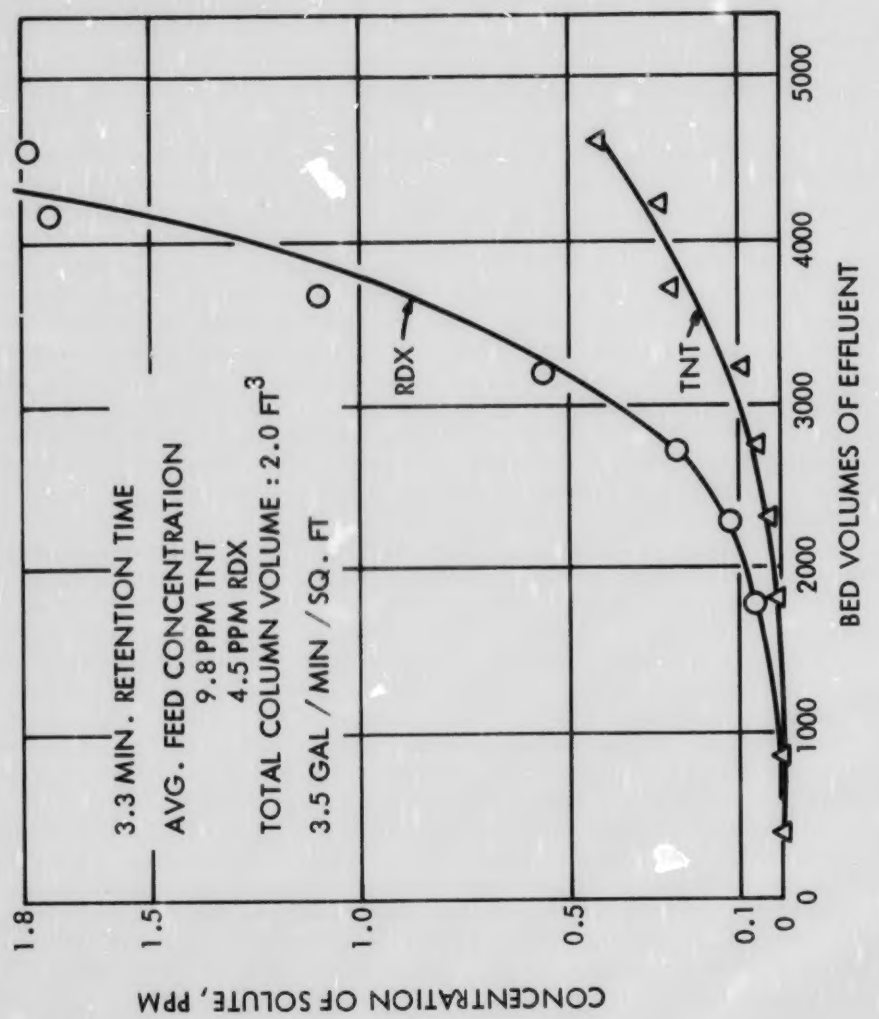

Figure 13 - Competitive Adsorption of RDX and TNT Using Filtrasorb 400 at Keyport Test Site

Station currently has a 20 gpm system planned, designed to reduce RDX below 1 mg/l (15zh). The carbon process would be most effective for wastewater devoid of TNT, such as the manufacturing wastewaters of Holston AAP, but would also be effective for wastewater containing TNT, although the treatment capacity for RDX would be much less than for effective TNT treatment. Since the activated carbon is not normally regenerated, effective RDX treatment would require excess carbon, and increase the overall cost of treatment.

48. Modifications to Current Treatment

a. Holston AAP, the manufacturing facility for RDX and HMX, has proposed to biologically treat these and other industrial process effluents from their Area B activities by aerated ponds (3f). There seem to be serious questions concerning the capability of biological treatment for RDX and HMX, however. In assessing the potential effectiveness of the proposed biological treatment at Holston AAP, the U. S. Environmental Protection Agency has pointed out that it is most unlikely that biological processes will degrade complex organic materials such as RDX and HMX (4a). A subsequent architect/engineer report to Holston AAP recommended treatment of Area B wastes by biological treatment (denitrification followed by trickling filtration), multi-media filtration, break-point chlorination and physical adsorption (5c). This latter process may be either activated carbon or synthetic resin.

b. Many studies have been made on the biological treatability of RDX and HMX. Osman and Klausmeier have reported, for example, no breakdown of RDX during studies on the microbial degradability of RDX, ammonium picrate and TNT (16o). Trickling filtration experiments with HMX at 2.2-2.5 mg/l resulted in effluent levels of HMX of 2.0-2.5 mg/l (14f). Green, studying explosives degradation in a 70 liter pilot activated sludge unit with 5 days hydraulic detention time, found only 14-42 percent reduction in RDX and 53.4 percent removal of HMX (2c). Pardee, in soil suspension tests, has reported partial breakdown of RDX. Repeated dosing of RDX to 7 to 19 mg/l, followed by degradation periods of 12 to 26 days, resulted in residual RDX levels below 3 mg/l (2c). Despite these results, U. S. Navy proposes to install a demonstration oxidation ditch at NAD McAlester for their Plant "B" wastes, the effluent of which is expected to contain less than 0.5 mg/l TNT and less than 0.5 mg/l RDX (14m). NAD McAlester has also planned a diatomaceous earth filter and activated carbon treatment system for their Plant "A" explosives contaminated wastewaters (14m).

c. Several LAP facilities have programs to install activated carbon treatment systems. These include Milan and Kansas AAP's, Yorktown Naval Weapons Station and NAD McAlester. Milan will treat wastewaters for their composition explosive melt-pour lines by activated carbon (31). Yorktown Naval Weapons Station will use a diatomaceous earth filter plus two carbon columns in series, and operate at 20 gpm wastewater flow. The Yorktown system is expected to produce effluent levels of 1 mg/l each of TNT, nitrocellulose and RDX (15zh). NAD McAlester also will use diatomaceous earth plus carbon treatment systems. Two complete systems are planned at McAlester, each with a treatment capacity of 80 gpm. System performance is expected to achieve 0.5 mg/l effluent TNT and RDX (14m).

d. Based upon the carbon performance and other data presented in paragraph 47 above, it is extremely doubtful that a carbon system treating TNT plus RDX can achieve equal effluent levels for both explosives (e.g., 1.0 mg/l for Yorktown or 0.5 mg/l for NAD McAlester). The preferential adsorption of and greater capacity for TNT displayed by activated carbon indicates that such treatment systems must be designed and operated on the basis of RDX treatment, and that this will perforce result in more rigorous treatment for TNT.

e. Kansas AAP also plans to use diatomaceous earth filtration plus carbon, for wastewater from melt-pour operations. However, wastewater from a detonator manufacturing operation, containing lead azide, lead styphnate and RDX, will be chemically treated. Sodium nitrite will be used to break down lead azide, and caustic to deactivate lead styphnate and RDX (1h(3)). Caustic hydrolysis of RDX reportedly occurs in 1-1/2 to 2 hours, yielding breakdown products of ammonia, formaldehyde and nitrite (2c).

f. Air Force Plant #78, which has wastewater associated with HMX use in LAP activities, including HMX grinding and incorporation, plans to dispose of wastewater from equipment cleanup and the HMX area laundry by discharge to catch basins, and ultimate disposal to evaporation/percolation ponds (15zk).

g. Beyond these activities, and the water management program associated with modernization of one of Holston AAP's five Composition B lines, no other types of treatment are programmed for implementation. Research is proposed however, to evaluate alternate treatment technologies.

49. Alternatives to Current Practice

a. The Army plans to investigate several methods of RDX and HMX control, in pilot scale studies at Holston AAP. Methods under consideration include: reverse osmosis; activated carbon adsorption; polymeric resin adsorption; and anaerobic biological degradation (3i). There are no existing data on RDX or HMX treatment by reverse osmosis or anaerobic degradation. The anaerobic digestion process is notable for its capability to degrade complex organic compounds, but is also generally recognized as a system extremely sensitive to toxicity. The toxicity of RDX and HMX has not been investigated to any significant extent (2c). The potential success of anaerobic degradation however will require low toxicity, plus capability of the anaerobic microbial population to degrade RDX and HMX.

b. The use of regenerable polymeric resin for RDX and HMX treatment would have a significant advantage over one-time use of carbon in terms of economics, if the resins are effective in removing the explosives. A novel approach is under investigation by NSWC White Oak, whereby RDX would first be concentrated and hydrolyzed on polymeric resin (14z). This approach is based upon preliminary studies which indicated that the relative adsorptivities of TNT and RDX were approximately the same on resin as on carbon, and further that the rate of alkaline hydrolysis by the resin, when on the hydroxide cycle, could be described by the equation,

$$\frac{d\,[RDX]}{dt} = k\,[RDX]\,[OH^-]$$

where k = 0.33 ± 0.05 moles/min (14z). The hydrolysis reaction, based upon experimental data, is reported to be (14z):

$$RDX + 3\,OH^- \rightarrow 0.99\,NH_3 + 1.26\,NO_2^- + 0.12\,N_2 + 1.13\,N_2O + xCH_2O$$

Others have reported that alkaline hydrolysis of RDX produces quantitatively two moles of nitrite (out of a possible three nitro groups) for each mole of RDX reacted. Alkaline hydrolysis of HMX produces 3 moles of nitrite out of a possible four nitro groups. Successful RDX treatment by alkaline hydrolysis has been reported (2c, 1h(3)). HMX has been noted to be more resistant to alkaline decomposition than is RDX, however (2c). The success of the adsorption plus hydrolysis process depends first upon the ability to concentrate RDX or HMX on the resin, and second upon the extent of hydrolysis achievable. A commercial resin, XAD, in bench scale tests, reduced RDX from an initial level of 45 mg/l, to below 0.02 mg/l (14z).

c. Results from recent pilot plant studies at NAD Hawthorne indicate however that the XAD polymeric resin is a much less effective adsorbent than activated carbon (14zb). The wastewater was treated by a sequence of air flotation, followed by a cooling tower. Effluent from the cooling tower was split into stream 1, which went through mixed media (sand and coal) pressure filtration followed by activated carbon adsorption; and stream 2 which passed through diatomaceous earth filtration followed by Rohm and Haas Amberlite XAD-4 polymeric resin adsorption. Table 30 summarizes the treatment results for TNT and RDX from several composition explosive wastewaters. For TNT, both carbon and polymeric resin provided effective treatment, consistently yielding effluent TNT levels below 0.5 mg/l. Activated carbon was even more effective for RDX, producing effluent levels of 0.02 mg/l or less. However, with the single exception of the Composition A-3 wastewater, the performance of the polymeric resin system was much less effective. Some RDX removal resulted in the first resin column, but no additional removal is seen for the second of the two series units. Table 31 summarizes overall treatment efficiency for Streams 1 and 2, based upon plant influent, and final plant effuent values. The results of this study indicate that activated carbon treatment is more reliable for RDX control, with the capability of reducing RDX to below 0.02 mg/l while simultaneously treating for TNT.

Table 30. Treatment for TNT and RDX by NAD Hawthorne Pilot Plant (14zb)

Explosive	Influent Concentration, mg/l	Flotation Effluent*	Cooling Tower*	Stream 1*		Stream 2*		
				Sand Filter	Activated Carbon	Diat. Earth	Resin Column-1	Resin Column-2
Comp. A-3								
TNT	11.4	81.9	620.0	434.2	< 0.5	422.5	4.35	< 0.5
RDX	79.9	82.8	72.3	87.9	0.02	-	0.62	< 0.01
Comp. B								
TNT	422	389	348	304	< 0.5	328	2.3	< 0.5
RDX	103	141.9	147.9	171	< 0.01	192.3	25.5	20.4
HBX - 1								
TNT	314	323	330	308	< 0.5	281	2.6	< 0.5
RDX	92.2	144.5	158.0	128.5	0.02	155.4	66.8	61.6
Mixture								
TNT	279	256	283	285.3	< 0.5	272.3	3.0	< 0.5
RDX	145.7	302.2	205.1	221.8	0.01	170.5	59.0	60.7

*Values given are for effluent from each treatment unit in mg/l concentration.

Table 31. Pilot Treatment Plant Efficiencies, NAD Hawthorne (14zb)

Wastewater	Constituent	Percentage of Removal	
		Stream 1*	Stream 2**
Comp. A-3	COD	92.5	32
	Suspended Solids	84	53.5
	TNT	90	13
	RDX	99.5	99.5
Comp. B	COD	97	91.5
	Suspended Solids	99.5	99.5
	TNT	99.5	99.5
	RDX	99.5	78
HBX - 1	COD	98	86.5
	Suspended Solids	98.5	97
	TNT	99.5	99
	RDX	99.5	30
Mixture	COD	97	83
	Suspended Solids	84	76.5
	TNT	99.5	99
	RDX	99.5	59

*Sand Filter/Activated Carbon
**Diatomaceous Earth/Resin

50. Impact of Air Pollution Control

a. Water scrubbers are widely used in melt-pour and other composition explosive handling steps. These scrubber systems generate wastewaters with characteristics similar to clean-up and other LAP wastewaters. For example, the wastewater reported in Table 24 for explosives packaging at Holston AAP results from dust control by an air scrubber system. At most facilities where air pollution control is not now employed, current plans are to use scrubber systems. NAD Crane, for example now uses scrubbers at their Rockeye Facility, and plans to install the same system at two bomb loading plants (14f). Scrubber overflow rates for these additional systems are estimated at 0.5 gpm per scrubber, with four scrubbers at each bomb loading plant. The major impact of scrubber installation is to increase total plant wastewater volume. Treatment processes applicable for other waste sources should apply equally well to the air pollution scrubber water.

b. As an alternative to wet-type scrubbers, Air Force Plant #78 has installed dry "absolute" filters for HMX grinding process dust control. This filter system, which will control particles down to 0.3 micron size, has a major advantage of not producing wastewater. The units used at Plant #78 (American Air Filter Co., Hospital Filter Units) are reported to be effective, and trouble free in operation (15zk).

51. Summary

a. RDX and HMX are manufactured at Holston AAP, and loaded at several Army, Navy and Air Force LAP facilities. The wastewaters associated with manufacture have been adequately characterized, although much less information is available on process wastewaters from LAP operations. Despite the lack of complete characterization data, specific treatment processes for these wastes have been selected at several plants.

b. Although Holston AAP does not currently treat wastewaters from RDX and HMX manufacture, biological treatment by an aerated lagoon is proposed. Prior attempts to biologically degrade RDX and HMX have been largely unsuccessful, and serious reconsideration is due the proposal of Holston AAP to treat the manufacturing wastewaters by an aerated lagoon.

c. More successful treatment has been achieved with activated carbon, such as for the Joliet AAP LAP wastewater. There is evidence to indicate that carbon may preferentially remove TNT, and carbon treatment processes designed for wastewaters containing both RDX or HMX, and TNT, should be designed for effective RDX or HMX removal. This might represent an over-design of the system for TNT treatment.

d. Although early work indicated that polymeric resin adsorption for RDX and HMX was promising, more recent pilot studies at NAD Hawthorne yielded inconsistent treatment results. Additional studies appear warranted however, in light of the possibility of polymeric resin regeneration or hydrolysis of RDX or HMX by the hydroxide form of anion exchange resins. With the exception of Air Force Plant #78, most LAP wastewater treatment systems under design or construction are based upon activated carbon treatment. Air Force Plant #78 will use evaporative ponds, as are now in use at both Milan AAP and NAVPRO Magna*. Such ponds are effective in semi-arid regions.

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*Also designated NIROP Magna.

SECTION VI - NITROGLYCERIN

52. Introduction

a. Nitroglycerin is used primarily as an ingredient of double-base and triple-base propellants. It is manufactured at Radford and Badger AAP's, NOS Indianhead and NAVPRO Magna. Nitroglycerin (NG) is manufactured by the batch process at Radford and Badger AAP's. Radford also has the newer continuous (Biazzi) NG process, as do both of the Navy facilities. The batch process at Radford is no longer in use, and the batch process at Badger is scheduled for replacement by the continuous process (3f). Thus, batch manufacture of NG will soon be phased out totally in the military munitions industry, being replaced by the Biazzi system.

b. The batch NG process employs three steps. In the first step, glycerol is added to a mixture of concentrated sulfuric and nitric acids. The nitration mixture is agitated, and cooled to hold the temperature below 25°C. After the reaction is completed the reacted product (a mixture of NG, dinitroglycerin (DNG), water, and spent sulfuric and nitric acids) passes to a gravity separator where the second step involves gravity separation of the NG from the nitration acids, and decantation of the NG. Spent acid is normally sent to recovery. In the final step, the NG is washed with aqueous sodium carbonate solution and water to remove and neutralize residual acidity. Several sequential water washes may take place. The NG is then taken to storage, usually in rubber lined carts, until used in propellant manufacture.

c. The continuous NG process is an automated system in which the nitroglycerin is produced by similar reactions to the batch process. At Radford AAP, for example, the Biazzi system incorporates the following steps (6e). The reaction components are first combined in a temperature controlled reacter. After nitration, the NG and acid mixture flows to an acid separator, where excess acids are removed. The NG then receives three 16-percent soda ash washes and two fresh water washes, to remove residual acids and impurities. The NG flows to an emulsifier where it is mixed with an equal volume of a three percent soda ash solution and conveyed to the NG storehouse. When the NG is retrieved from the storehouse, the emulsifying solution is decanted to catch basins, to remove non-soluble NG by gravity settling.

53. Waste Sources

a. Wastewater flows from NG manufacture result from the soda-ash solution and water washes following the nitration step, and from NG storage when dilute soda-ash solution is decanted before NG use. The only batch NG process in operation is at Badger AAP. Table 32 presents wastewater characteristics for this operation. For comparision, average wastewater characteristics for batch NG manufacture in the commercial explosives industry are also included in Table 32 . No data on nitroglycerin content of the Badger AAP wastewater flow are available. For

Table 32. Wastewater Characteristics of Batch Nitroglycerin Production

Parameter*	Badger AAP (1a(3))		Commercial Explosives Industry (4d)
	Range**	Average	
Flow, MGD	0.06-0.17	0.11	0.0097
pH	1.7-9.5	4.7	2.7-10.0
Temperature, °C	10-19.4	14.6	-
Kjeldahl-N	1.1-5.1	2.5	23.0
Nitrate-N	0.5-200	116.6	5564
Sulfate	62-415	242.6	3154
COD	18-340	109.1	2260
Nitroglycerin	-	-	315-12,700
Sodium	-	-	13,323

*All parameter values in mg/l except flow, pH and temperature.
**Maximum and minimum values taken from four-hour composites.

commercial explosives plants, NG content of manufacturing wastewater ranges from 315-12,700 mg/l. The nitroglycerin content of process wastewater will represent both soluble NG and NG present above the solubility limit. Nitroglycerin solubility in water at 15°C is 1,270 mg/l (16zu).

b. The pH of wastewater from NG manufacture ranges from low for the first (sour water) wash after nitration, to alkaline for subsequent washes with sodium carbonate to neutralize residual acidity. In addition, the wastewater is high in nitrate and sulfate from the nitration acid mixture, and COD from the organic reactants and products of NG manufacture.

c. Waste characteristics for the continuous Biazzi NG process at Radford AAP are presented in Tables 33 and 34. Other flows associated with NG manufacture are a 15,000 gpd flow for the air compressor building and a 20,000 gpd flow from the glycerin soda solution refrigeration house. These latter two flows are noncontact and contain no explosives contaminants (6e). These two flows are currently combined with wastewater from the nitration house and discharged to the receiving water. The manufacturing wastewater (Table 33) is notably high in sulfate, nitrate, alkalinity and dissolved solids. Nitroglycerin averages 1,300 mg/l in the wastewater, while dinitroglycerin averages 850 mg/l. The COD is also high, reflecting in part the NG and DNG content. NG and DNG have, respectively, theoretical COD's of 0.8 and 1.02 mg COD/mg NG and DNG. While DNG gives 100 percent of the theoretical value in the COD test, NG yields only 18.5 percent (3u). Thus, NG plus DNG account for 86 percent of the COD value in Table 33, but only 19 percent of the COD value in Table 34. The NG store house waste represents only 5000 gpd and is more alkaline than the manufacturing wastewater. In other constituents, the storehouse waste is similar but more dilute.

d. No wastewater characterization data are available for NG manufacture at NAVPRO Magna or NOS Indianhead. However, both facilities use the continuous Biazzi process, and the wastewaters should be similar to data presented in Table 33. At NOS Indianhead, an extensive and comprehensive environmental monitoring program, titled the Navy Environmental Protection Data Base (NEPDB) Program has recently been initiated. The program involves sampling at nine stations on the facility for a variety of standard pollution parameters such as BOD, heavy metals and oil and grease. A future monitoring program will extend to analysis for explosives pollutants such as NG, DNG or nitrocellulose and to characterization of individual process effluent streams (15zl, 14zc, 14zr).

54. Effects of Water Management

a. A water management program proposed for the Radford AAP continuous NG process would reduce wastewater discharge by 64 percent, from 50,000 to 18,000 gpd (6a). The program incorporates the following components:

Table 33. Combined Wastewater Characteristics of Radford AAP Continuous NG Nitration and Spent Acid Buildings 9463 and 9466 (6e)

Parameter*	Range	Average
Flow, MGD	-	0.015
pH	8.4-9.2	8.6
BOD	1.5-6.5	4.5
COD	1,000-1,400	1,228
Nitrate-N	7,500-20,000	13,280
Sulfate	534-3,550	1,416
Total Alkalinity ($CaCO_3$)	9,000-16,400	12,700
Suspended Solids	3.0-63.3	23.0
Dissolved Solids	68,000-98,950	81,626
Nitroglycerin	800-1,800	1,300
Dinitroglycerin	520-1,180	850

*All parameter values in mg/l except flow and pH.

Table 34. Wastewater Characteristics of Radford AAP
NG Store Houses 9471 and 9472 (6e)

Parameter*	Range	Average
Flow, MGD	-	0.005
pH	10.2-11.3	10.5
BOD	2.4-4.1	3.2
COD	460-1456	912
Nitrate-N	270-665	477
Sulfate	20-179	130
Total Alkalinity ($CaCO_3$)	7,500-18,000	11,400
Suspended Solids	3.3-22.1	11.3
Dissolved Solids	2,952-30,848	13,905
Nitroglycerin	83-490	266
Dinitroglycerin	41-248	130

*All parameter values in mg/l except flow and pH.

(1) Installation of a refrigeration unit at the glycerin soda solution refrigeration house. Net water savings amounts to 20,000 gpd.

(2) Use of 10,000 of the 15,000 gpd cooling water flow from the air compressor house as washwater for spent acid wash. Net water savings are 10,000 gpd.

(3) Use of the first washwater from NG manufacture (after the soda-ash solution neutralization step) as emulsifier water from NG storage. Net water savings are 1200 gpd.

(4) Reuse for NG storage water, after adjustment of the soda ash content to 16 percent, as the first neutralization wash. Net water savings amounts to 1200 gpd.

The wastewater discharges remaining, after implementation of this program, would include the remaining 5000 gpd of air compressor cooling water flow which contains some oil, a 10,000 gpd flow from spent acid washing, a 1200 gpd 16% soda-ash neutralization flow, 420 gpd clean-up water and 1575 gpd (winter only) in-line heating water (6a). The net change in actual process contaminated water involves reduction from a present flow of 14,000 gpd to 11,600 gpd, with the balance due to savings in non-contact water use. The process water use reduction is thus 2,400 gpd, due to sequential use of a single 1200 gpd flow as first NG washwater, second NG emulsifier (storage) water and finally for soda-ash supplemented NG neutralization.

b. The water management program proposed for Radford AAP is not unique to the manufacture of NG by the continuous Biazzi process, and would be equally effective for both the batch process at Badger AAP and the Biazzi process at NOS Indianhead.

55. Current Treatment Practice

a. Process wastewater at all production facilities are routed through catch basins, for removal of non-soluble nitroglycerin. At Radford AAP, these catch basins have been reported to contain very little accumulation of solids (1n(3)). At both Radford AAP and NOS Indianhead, the catch basin overflow is discharged without further treatment (3f, 15z1).

b. Badger AAP uses percolation/evaporation ponds for final disposal of the NG process wastewater. At Badger, all wastewater from the NG manufacturing area flows to two percolation ponds, where the liquid leaches into the ground (1a(3)). The combined wastewater flow to the pond is reported to have an average pH of 4.7, average nitrate-N concentration of 117 mg/l and average sulfate concentration of 240 mg/l. The ponds have sandy bottoms and the leaching system is reported to operate effectively (1a(3)). At 25 percent capacity production of NG, the ponds receive 120,000 gpd of wastewater (2b).

c. NIROP Magna follows a similar program for wastewater disposal. Nitroglycerin manufacture wastewater is discharged to earthen sumps. There is some removal by percolation and substantial evaporation. However, twice per year the sumps are allowed to dry up, and the sediments decontaminated for residual NG and DNG by placing explosives in the bottom of the sumps and detonating the explosives. A similar procedure has been employed at one commercial explosives plant (4d). Many commercial NG plants also treat their acidic wastewater for pH, by percolation of the waste through crushed limestone beds or other neutralization techniques (4d).

56. Modifications to Current Treatment

a. Among the four nitroglycerin-producing facilities, only Radford AAP has a program for additional treatment. Current plans, in addition to water management efforts, include installation of a guttering system to collect the wastewater at specific processing buildings and direct it to primary clarifiers to remove settleable solids, grit and oily material such as insoluble NG. The clarified effluent will be treated with caustic and sodium sulfide, to decompose NG and DNG (15zp). The effluent will then be treated in a 250,000 gpd secondary treatment process (6a). An activated sludge system is proposed as the secondary treatment method (3f). The collection and treatment facilities at Radford have been funded (4c).

b. Some success has been achieved with biodegradation of nitroglycerin (3h). Preliminary laboratory work with wastewaters from NG production indicates that some components are readily biodegraded, but it has been reported that at least one component of the wastestream is recalcitrant to direct biological attack (3h). Based upon oxygen utilization respirometry studies at Radford AAP, this recalcitrant constituent appears to be NG. Standard substrate solutions to which DNG was added showed higher oxygen utilization rates than for the standard substrate alone, while rates were depressed in standard solutions to which NG had been added (6a).

c. Further, nitroglycerin is reported toxic above 600 mg/l (15y). In another study on nitroglycerin manufacturing effluent, gravity clarification yielded NG levels of 900 to 2100 mg/l. This waste was treated by activated sludge (16zt). At 16 hours aeration time, successful treatment was achieved, with a decomposition product of nitrite. The maximum concentration of NG which could be treated by the activated sludge process was 400 to 500 mg/l (16zt). The evidence thus indicates that biological treatment of high NG wastewaters, such as described in Tables 32 and 33, is not feasible without dilution or pretreatment for NG removal. Further, the proposed biological treatment system would not control the high nitrate, sulfate and alkalinity levels of the wastewater.

57. Alternatives to Current Practice

a. Various treatment methods have been investigated for control of NG and DNG. Physical processes studied include: reverse osmosis;

adsorption on to polymeric resins; and activated carbon adsorption. Chemicals investigated for treatment include: lime saponification; oxidation with ozone or permanganate; and reduction with sulfide salts.

b. Preliminary results of research studies at Radford AAP indicated that reverse osmosis is capable of removing NG and DNG (6a). These results have not yet been confirmed in pilot studies. The extreme pH values associated with acid washing and soda ash neutralization during NG manufacture would likely be detrimental to reverse osmosis cellulose acetate membranes. Thus, pH adjustment prior to reverse osmosis treatment would be necessary. In addition, the cellulose acetate membrane adsorbs and becomes saturated with NG (3u). Reverse osmosis treatment using currently available membranes thus does not appear feasible.

c. Studies at Radford indicated that activated carbon adsorption of NG was not feasible, but that adsorption on polymeric resins was possible (6a). In reticulated resin adsorption column tests, using Rohm and Haas resin XAD-4, NG removal was excellent, but DNG removal only fair (6a). The resin requires regeneration with ethyl alcohol or other organic solvent.

d. Lime and caustic have been reported successful as chemical treatment techniques for NG. Nitroglycerin is hydrolyzed very slowly at neutral pH. It also reacts rather slowly in concentrated caustic (1.5% NaOH), with a reported decomposition rate of 0.24 per mole-second (2b). Decomposition of NG with lime, at a lime dosage of 2 gm/l, is reported to require up to three days, yielding decomposition products of calcium sulfate, calcium sulfite and calcium salts of low molecular weight organic acids. The treated waste has a high residual pH (15zt). Saponification of NG wastewater with lime at pH 11 has been reported at Radford to yield nitrate, plus glycerin which could be treated biologically (15x). In addition to decomposition of NG, the use of lime, plus calcium chloride or calcium sulfate, would have an additional advantage by reducing the high alkalinity of the wastewater. The pertinent reactions to remove alkalinity by precipitation are given below.

$$2\ NaHCO_3 + Ca(OH)_2 \rightarrow CaCO_3 + Na_2CO_3 + 2H_2O \qquad [1]$$

$$Na_2CO_3 + CaSO_4 \rightarrow CaCO_3 + Na_2SO_4 \qquad [2]$$

Calcium carbonate is precipitated in each of the reactions, thereby reducing the carbonate alkalinity. In laboratory studies at Radford AAP on this process, alkalinity was reduced from 16,400 to 70 mg/l. Addition of anionic polymer resulted in effective precipitate sedimentation (6e). Based upon these results, approximately 70 lb of lime and 140 lb of calcium sulfate are required per 1000 gallons of wastewater to reduce alkalinity to acceptable levels (6e). Calcium carbonate sludge sedimentation can be accomplished within five minutes with addition of 5 mg/l anionic polymer flocculant.

e. By adding excess lime in the alkalinity precipitation experiments, resulting in higher pH, complete NG and DNG decomposition occurred within 30 minutes at pH above 11 (6e). The excess lime required would be about 20 additional lbs per 1000 gallons of wastewater. The Radford study indicated that removal of alkalinity, plus decomposition of NG and DNG in a single treatment step were possible (6e).

f. Both ozone and permanganate have been studied as oxidants for decomposition of NG and DNG. Permanganate dosages up to 200 mg/l, at reaction times of one hour, resulted in only about 40 percent decomposition of NG and essentially no removal of DNG (6e). Although higher permanganate dosages would likely improve NG treatment, the method does not appear to be economically feasible at the high dosages necessary for NG, and, in any case, is ineffective for DNG.

g. Laboratory-scale ozonation studies indicate effective decomposition of both NG and DNG, at long reaction times and high ozone dosage. NG nitration wastewater, after lime plus calcium sulfate treatment for removal of alkalinity, was treated with ozone at an ozone addition rate of 4160 mg/hr ozone per liter of wastewater. During the first ten minutes of treatment 100 percent of the ozone bubbled through the treatment column was consumed, but during the remaining three hours of treatment only 1000 to 1400 mg/hr/liter were consumed in the oxidation reaction. Ozone treatment at pH values of 4.9, 7.2 and 8.6 indicated that pH had little effect on ozone treatment. At six hours treatment time and pH 4.9, NG at 324 mg/l and DNG at 122 mg/l initial concentrations were completely decomposed (6e). The ozone requirement was 23 mg ozone per mg NG and DNG.

h. Sodium sulfide solution has been used for many years to decompose NG during equipment cleanup (4g). In studies at Radford AAP, NG nitrator wastewater was treated with sodium sulfide dosages of 100 to 700 mg/l. Initial NG and DNG concentration of 351 and 122 mg/l, respectively, were totally decomposed within 30 minutes at sodium sulfide dosage of 320 mg/l (6e). Treatment pH was 8.6. These results indicate that in terms of treatment, chemical dosage and reaction time required, lime treatment and sodium sulfide treatment yield equivalent results. Table 35 presents a comparison of treatment chemical costs for lime, permanganate, ozone and sulfide treatment. On the basis of total cost, sulfide treatment is most economical. However if removal of alkalinity is also required, single-step lime plus calcium sulfate removal of alkalinity plus NG and DNG becomes most economical. The major disadvantages of this treatment technique are the volumes of calcium carbonate sludge generated which must be disposed of, and the added soluble sulfate from calcium sulfate treatment chemical use.

i. There are certain potential problems associated with the use of sulfide as a treatment chemical, including the possibility of residual toxic sulfide ion in the effluent. Further, sulfide treatment of wastewater which contains insoluble NG may represent an explosive hazard, since the saponification and reduction reactions are exothermic.

Table 35. Treatment Chemicals Cost for Nitroglycerin Manufacturing Wastewater Treatment (6e)

Treatment	Cost per 1,000 gal
Lime-Calcium Sulfate Treatment	
a) For Alkalinity Only	$ 2.38
b) Increment for NG and DNG Decomposition	$ 0.18
c) Total Cost	$ 2.56
Polymeric Resin (Regeneration by ethanol)	$10.00
Ozone Oxidation	$38.50
Sodium Sulfide Decomposition	$ 0.81

With concentrated NG, where the heat of reaction is not dissipated, danger of explosion due to thermal shock has been cited (4g). In addition, the sulfide treatment method is reported to liberate sulfur compounds with a very disagreeable pungent odor (4g). Despite these factors, the sulfide decomposition process has been selected for treatment of NG wastewaters at Radford AAP (15zp).

58. Summary

a. Wastewaters from nitroglycerin manufacture are common to both the military and commercial explosives industries. The wastewaters typically vary in pH from acidic to alkaline, and are high in NG, DNG, nitrate and sulfate. Current treatment is limited to catch basins, with final discharge to waterways or evaporative ponds. Although several treatment processes have been proposed, most are ineffective for NG, DNG or both. Only sulfide decomposition is proven, and Radford AAP plans to use sodium sulfide treatment followed by activated sludge.

b. However, there are several undesirable side-effects of sulfide treatment, including: the presence of residual toxic sulfide ion in the process effluent; the liberation of disagreeable odors during sulfide decomposition; and the possibility of explosive hazard due to exothermic reaction. These aspects of sulfide treatment indicate that new research and development efforts should be undertaken to assess alternative processes for both decomposition and recovery of NG and DNG.

SECTION VII - SELLITE

59. Introduction

Sellite (sodium sulfite) is manufactured at Volunteer and Joliet AAP's. It is used in the purification of crude TNT to remove unwanted isomers, leaving α-TNT. Sellite is manufactured by burning sulfur to produce sulfur dioxide, SO_2. The product gas is countercurrent scrubbed with water to remove sulfur trioxide and other impurities, followed by absorption of SO_2 by a solution of sodium carbonate (soda ash) in a countercurrent packed tower. The sodium sulfite effluent from the tower is recirculated through the SO_2 absorption tower until the desired sellite strength (16% Na_2SO_3) is obtained. This solution is then used in TNT purification. Figure 14 is a schematic of sellite manufacture.

60. Waste Sources

a. Wastewaters from sellite manufacture result from overflow from the gas scrubber water tank, spills of soda ash and sellite solutions, and floor washings and spill clean-ups (8f). The sellite effluent is characterized by a widely fluctuating pH, low dissolved oxygen, and high concentrations of ash, sulfate, sulfite and total dissolved solids. This waste flow discharges into a small lagoon where it is aerated and neutralized, and is then discharged. Waste flow, with one of the two sellite manufacturing units at Joliet AAP in operation, has been reported as ranging from 0.062 to 0.614 MGD with an average flow of 0.222 MGD. Flow during this period of measurement was strongly influenced by rainfall runoff into the effluent ditch (1g(3)). An average flow of 0.173 MGD results if flow measurements on days of heavy rainfall are disregarded (1g(3)). A separate study of sellite wastewater discharge indicated a range of 0.058 to 0.737 MGD, with an average flow of 0.213 MGD, or 148 gpm (3b). The estimated actual process effluent per sellite manufacturing unit has been estimated at 0.062-0.125 MGD, exclusive of surface runoff (8d).

b. Limited data are available on the process effluent prior to neutralization, lagooning and aeration. Table 36 presents available data. The data indicate an anoxic discharge which at the average flow rate of 148 gpm represents 227 lbs/day COD, 1246 lbs/day sulfate and 1694 lbs/day sulfite. The anoxic condition of the wastewater results from the reaction of sulfite with dissolved oxygen to produce sulfate. The data of Table 36 were collected during summer months (June and July), and in cooler months, the effluent contains trace amounts of dissolved oxygen (3b).

61. Current Treatment Practice

Wastewater discharged from sellite manufacture is currently treated by pH adjustment with soda ash, followed by oxygen addition by only one mechanical surface aerator in a small flow-through lagoon. The lagoon

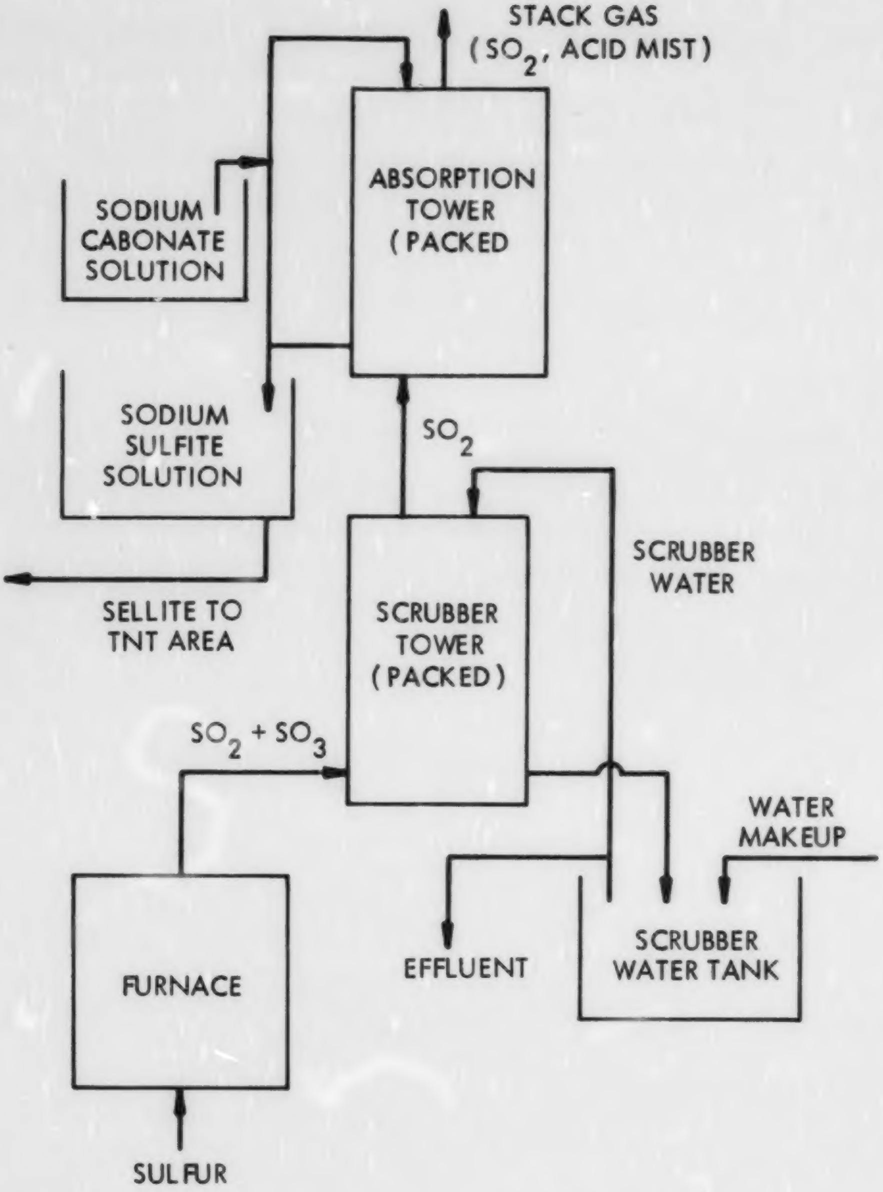
STACK GAS
(SO_2, ACID MIST)
SODIUM CABONATE SOLUTION
ABSORPTION TOWER (PACKED
SODIUM SULFITE SOLUTION
SO_2
SCRUBBER WATER
SELLITE TO TNT AREA
SCRUBBER TOWER (PACKED)
$SO_2 + SO_3$
WATER MAKEUP
EFFLUENT
SCRUBBER WATER TANK
FURNACE
SULFUR

Figure 14 - Sellite Manufacture at Joliet AAP (15zb)

Table 36. Sellite Wastewater Characteristics Before Treatment (3b)

Parameter*	Range	Average
pH	2.3-3.5 (minimums)	2.3-5.6
COD	17-493	128
Dissolved Oxygen	0.0	0.0
Sulfate	287-2410	701
Sulfite	450-2260	953
Flow, gpm	40-512	148

*All in mg/l, except pH and flow.

effluent is discharged without further treatment. Tables 37-39 summarize effluent characteristics from the lagoon, as a result of three separate monitoring studies. Table 39, presenting both lagoon influent and effluent data, indicates that the lagoon system is ineffective in producing an effluent of acceptable pH and dissolved oxygen concentration, although sulfite is 96 percent removed in the aeration process. Since sulfate concentration does not increase by a stoichiometric equivalent to the reduction of sulfite, removal may result from air stripping of sulfur oxides, as well as oxidation of sulfite. The dissolved oxygen data of Table 39 are somewhat atypical, since results of additional monitoring efforts on lagoon effluent revealed effluent dissolved oxygen levels of 0.4 to 10.6 mg/l when the surface aerator was in operation, with oxygen levels below 3.0 mg/l occurring only 27.7 percent of the time (3b). With the aerator not operating, the lagoon effluent oxygen ranged from 0.0-3.0 and averaged 0.6 mg/l. Thus, mechanical aeration does improve effluent oxygen and sulfite levels, but it is likely that additional aeration capacity is required to provide more consistent results.

62. Modifications to Current Treatment

a. In order to provide more effective and consistent treatment for sulfite, longer aeration periods and additional mechanical aeration capacity are required. The present surface aerator has a rated capacity of 14 lb/hr oxygen input, and is estimated to be operating near rated capacity (3b). To achieve a consistent effluent dissolved oxygen level of 3 mg/l, added capacity of 8 lbs/hr oxygen input is reported necessary (3b). The performance of the lagoon system would also be enhanced by flow equalization, as indicated by the almost 13-fold variation in flow rate shown in Table 36.

b. Poor pH control is evidenced by all available data (Tables 37-39), but inadequate treatment has been ascribed to equipment malfunction rather than poor process design (3b). The pH system is set up for proportional control, which yields imprecise control capability. Improved performance would result from installation of a feed-forward control system, and the effluent should be monitored by an alarm, to warn of equipment malfunction.

c. No attempt is made to control effluent sulfate, which has been reported to reach 1750 mg/l (Table 38). Current pH control is with soda ash, which yields soluble reaction products. Use of lime would be equally effective in neutralization, given the detention time of the lagoon system, and might have the additional benefit of partially removing sulfate by precipitation of calcium sulfate.

63. Summary

In summary, the type of technology applied to sellite wastewater is appropriate, with the possible substitution of lime for soda ash in neutralization. Treatment deficiencies result from inadequate treatment system aeration capacity and detention time, plus poor neutralization performance, rather than other factors.

Table 37. Sellite Wastewater Treatment System Effluent Characteristics (1g(3))

Parameter*	Range	Average
Temperature, °F	65.0-79.0	72.0
pH	2.1-7.8	5.3
Acidity	9.0-720.0	209.7
Alkalinity	0.0-382.0	125.0
Total Solids	824-2030	1453
Suspended Solids	1.0-40.0	17.1
Dissolved Solids	784-2015	1438
TOC	6.0-10.2	8.5
Sulfate	530-1400	928.6
Sulfite	10.0-1600	330

*All in mg/l, except pH and temperature.

Table 38. Sellite Lagoon Effluent Characteristics (8d)

Parameter*	Range	Average
Temperature, °F	63-73	71.3
pH	3.3-9.8	7.1
Color	5-50	36.0
Turbidity	3.3-150	24.7
Hardness	190-449	342.1
Dissolved Oxygen	0.0-10.3	4.3
BOD_5	0.0-94.7	12.7
COD	8.0-199	44.4
Sulfate	398-1750	752.8
Chloride	39-301	105.6
Sodium	137-1350	471.3
Suspended Solids	2-37	19.7
Dissolved Solids	338-11,806	2408

*All in mg/l, except pH and temperature.

Table 39. Comparison of Lagoon Influent and Effluent Sellite Wastewater Characteristics (3b)

Parameter*	Influent	Effluent
pH	2.3-5.6	4.3-10.0
Dissolved Oxygen	0.0	0.0
COD	128	38
Sulfate	701	1008
Sulfite	953	35

SECTION VIII - PROPELLANTS

64. Introduction

a. Propellants may be divided into three classifications: solvent, solventless and composite. There are many variations in formulations of propellants within each classification. Solvent propellants include single and multi-base compositions with NC as the major ingredient plus stabilizers and catalysts. Double base propellants incorporate nitroglycerin, while triple base propellants include both nitroglycerin and nitroguanidine. The basis for the solvent classification is the use of one or more NC solvents in the formulation process. Solventless propellants also contain NC plus typical ingredients of solvent propellant, but are blended in a water-wet state without addition of organic solvent. Composite propellants contain, in addition to typical double-base ingredients, significant amounts of oxidizers such as ammonium perchlorate or HMX, plus powdered aluminum. Additionally, composite propellants are based on a variety of organic binders, substituted for the double-base matrix of NC-NG. The latter types of composite propellants are discussed in Section IX.

b. Solvent propellant manufacture produces smokeless powder, powder which may be extruded into solid rocket motors, and casting powder for composite propellants. Solventless propellant is produced as a "carpet roll," which may be extruded into solid rocket motors, or cut into mortar increments. Casting of composite propellant is more properly a loading then manufacturing operation and, as such will be discussed in Section IX of this chapter.

c. The wastewaters of propellant manufacture reflect both the constituents of the products, and the blending process (e.g., solvent vs. solventless). Wastewater treatment technology for propellants will be discussed in separate sections below, according to the two-propellant classification of solvent and solventless.

SECTION VIII-A - SOLVENT PROPELLANTS

65. Introduction

For purposes of waste characterization and evaluation of treatment technology, solvent propellants will include single and multi-base propellants, and ball powder. Ball powder production is a special form of the solvent process. Badger AAP is the only military plant which manufactures ball powder (3a).

66. Waste Sources

a. The process steps are essentially the same in the production of solvent-type single, double and triple base propellants.

Major differences are in the specific chemicals and explosive ingredients added. In batch single base propellant manufacture, nitrocellulose is shredded and then mixed with ethyl alcohol, to dehydrate the NC and form a colloidal dough which is pressed into blocks. Pressing yields a weak alcohol solution. The blocked dough is then blended thoroughly with ethyl ether, DNT and other ingredients, depending upon the exact formulation desired. The dough is blocked once again and then extruded through dies, resulting in strands having a fixed number of perforations. The strands are cut to a specified length and transferred to a solvent recovery area.

b. In the solvent recovery area, the cut powder is washed with water previously heated to 60°C. This step partially removes residual solvents and DNT from the perforations within the pellets. After the water wash is completed the pellets are purged with methane gas, to remove final traces of solvents. Solvents are recovered from the methane (16zw). The powder is then air dried. The manufacture of double base solvent propellant is similar to the single base, with the addition of several processing steps for adding nitroglycerin and other chemicals for the formulations desired. Nitroglycerin composite double-base propellants require additional processing steps for the blending of ammonium perchlorate, HMX and powdered aluminum.

c. Triple base propellant production is a somewhat more complicated operation. About 400 lb of propellant is made per batch (2c). After shredding and dehydration, nitrocellulose is mixed with nitroglycerin and acetone to form a pre-mix slurry. About 200 lb of nitroguanidine blended with about 4 lb of ethylcentralite, a stabilizer and waterproofing agent, is slowly added to the pre-mix and blended. Inert gas is bubbled through the mix to remove volatile solvents, until the mixture reaches the desired viscosity. The dough is then blocked and extruded through dies, and the strands cut. Twenty pound batches of propellant are placed in trays and forced air dried. The triple base propellant grains are then glazed with graphite prior to packout (2c).

d. At NOS Indianhead, NC is purchased either water-wet or alcohol-wet. If obtained water-wet, the water is pressed from the NC, which is then rewet with ether. Subsequent processing steps, to manufacture double-base propellant, are as described previously (15z1).

e. Alcohol solution from the dehydration and first blocking steps is recovered by a rectification (distillation) process (1n(3)). The weak alcohol solution is passed through a steam purged still, with alcohol vapor recovered at the top and condensed. Steam condensate and residual still liquid are discharged as wastewater from the bottom of the still (1n(3)).

f. Volumes of wastewater generated in single and multi-base propellant manufacture are relatively small, and consist almost entirely of cleanup water from shift and weekly equipment cleanup and floor washdown operations. Screens, dies and often metal objects which have come into contact with propellant are cleaned by chemical digestion, using concentrated sodium hydroxide. In this operation the screens, dies and metal parts are hand packed into a wire basket. The cleaning tank is charged with 500 gallons of a twenty percent sodium hydroxide solution and heated to 217°F. The basket is then lowered into the cleaning tank. After completion of the digestion process, the basket is removed, drained and lowered into a rinse tank where the parts are cooled and rinsed in 500 gallons of rinse water. When the cleaning operation is completed, the water from both tanks is discharged (6a). Currently, at Radford AAP, the spent caustic is blended into the TNT red water (6a). This caustic solution is reported to total 1,200 gpd (3f). A similar discharge at NOS Indianhead is reported to range from 20-300 gpd (15z1).

g. Limited data are available on waste volumes associated with single and multi-base propellant manufacture and clean-up operations. Table 40 summarizes data from Radford AAP. The data, taken from three sources, do not show agreement in waste volumes. For example, average daily volumes of 500 and 86,000 gpd have been reported for single base propellant manufacture at Radford AAP (1n(3), 6e). The larger volume incorporates an unknown portion of cooling water, however. Tables 41 and 42 present wastewater characteristics, for single and multi-base propellant manufacture, for the high and low discharge volumes given in Table 40. Despite the differences in reported flow volumes for the two data sources, there is little difference in the concentrations of individual constituents. As shown in Table 41, the larger reported flow contained higher levels of total organic carbon and COD, while in Table 42, the reverse situation holds. Beyond these two parameters, plus nitrate for single base, there is little to differentiate between the wastes.

h. The heated water used to partially remove residual solvent from the extruded and cut powder, referred to as "water-dry waste," is diluted with cooling water and discharged at Radford AAP (16zw). This waste is reported to contain significant quantities of ethyl alcohol, diethylether and DNT. Table 43 presents characteristics of this waste, prior to dilution with cooling water. Although the data are limited, the high organics level does indicate the presence of solvents at significant concentrations.

i. A further wastewater source is propellant conveyance water in the propellant sorting operation. Table 44 summarizes waste characteristics for the Radford AAP propellant sorting process.

j. One further source of wastewater from solvent propellant manufacture is the solvent recovery process, for recovery of alcohol from the dehydration water. Recovery of alcohol by distillation results in a residual wastewater consisting of still bottoms. These still bottoms, from two rectification units at Radford AAP, are reported as 21,100 and 8,640 gpd respectively. In addition, there is a cooling water discharge for each alcohol rectification unit of about 430,000 gpd (1n(3)).

Table 40. Wastewater Volumes for Solvent Propellant Manufacture at Radford AAP

Propellant	Wastewater Volume, gal		Reference
	Daily Average	Periodic Washdown	
Single Base	500 86,000*	3,700	ln(3) 6e
Multi-Base	660 74,000*	4,960	ln(3) 6e
Combined	5,000		4c

*Includes some cooling with process water.

Table 41. Wastewater Characteristics of Single Base Propellant Manufacture at Radford AAP

Parameter	Concentration (1n(3))*		Concentration (6e)*	
	Average	Range	Average	Range
Flow, gpd	500	-	86,000	-
Temperature, °F	65.9	56-80	69.2	60-77
pH	8.7	7.6-10.0	7.6	6.7-8.7
Total Solids	2233.6	10-25,358	262	10-1068
Suspended Solids	8.1	1-161	6.9	1-21
Total Organic Carbon	29.9	5-420	83.7	5-777
COD	43.9	10-195	627.4	10-8755
NO_2 + NO_3 Nitrogen	159.4	0.1-1920	5.4	0.4-21.6
Ethyl+Diethyl Ether #	4.1	4.0-7.0	-	-

*All units in mg/l except flow, temperature and pH.

#As reported by U.S. AEHA.

Table 42. Wastewater Characteristics of Multi-Base Propellant Manufacture at Radford AAP

Parameter	Concentration (ln(3))*		Concentration (6e)*	
	Average	Range	Average	Range
Flow, gpd	660	-	74,000	-
Temperature, ^{o}F	-	-	78	53-90
pH	7.95	7.3-8.7	7.6	3.2-8.9
Total Solids	472.4	57-1677	637	70-1805
Suspended Solids	31.6	12.5-67	16	0-45
Total Organic Carbon	1012.0	7-5300	10	2-56
COD	194.5	17-510	107	5-1195
NO_2 + NO_3 Nitrogen	4.4	0.25-17.3	11.6	4-73

*All units in mg/l except flow, temperature and pH.

Table 43. Characteristics of Water-Dry Waste from Radford AAP (6e)

Parameter	Range	Average
Flow, gpd	-	15,000
Temperature, °F	155-165	150
pH	6.55-7.75	7.26
COD, mg/1	593-28,600	7,295
TOC, mg/1	96-3525	1,011
NO_3-Nitrogen, mg/1	5-45	19

Table 44. Characteristics of Propellant Conveyance Wastewater at Radford AAP (6e)

Parameter	Range	Average
Flow, gpd	-	210,000
Temperature, °F	60-79	69
pH	7.4-8.6	7.7
Total Solids, mg/1	91-226	130
COD, mg/1	85-478	174
TOC, mg/1	14-71	30
NO_3-Nitrogen, mg/1	3.5-13.0	8.0

Still bottom waste characteristics for Radford and Badger AAP's are presented in Table 45. The pH of the still bottoms is maintained near neutrality by pumping an 8 percent caustic solution into the lower section of the still (1n(3)). The addition of caustic serves to decompose NC fines in the still bottoms (1a(3)). The wastewater at Radford AAP is discharged, after dilution with cooling water, to the Radford C-Line Acid Neutralization Facility (1n(3)). Cooling water accounts for 97 percent of the total flow for the alcohol rectification area and the combined flow, as a result of the high dilution of still bottoms by cooling water, is relatively uncontaminated.

k. A comparison of the two Radford discharges described in Table 45 suggests that the discharge of Bldg. 1502 was diluted prior to the point of sample collection. This conclusion is substantiated by the fact that the second discharge is up to three hundred times more concentrated in solids than the first. Notably high, in addition to solids, is organic matter. The wastewater would also be expected to contain residual NC and NC decompositon products. With the exception of higher average pH and nitrogen, the Badger AAP discharge is intermediate to the two Radford discharges.

l. The manufacture of ball powder, a double base solvent propellant, at Badger AAP involves processing steps and compounds not used in other solvent propellants. Nitrocellulose is ground and washed in benzene plus ethylacetate to extract impurities. The benzene is removed by decantation, followed by vacuum distillation. The purified NC in ethylacetate is then shaped into uniform balls in a second still. Sodium sulfate and collagen protein is added to the solution to prevent ball agglomeration during the distillation step. The solvent is boiled off, and the ball powder is washed, size separated by wet screening, impregnated with NG, washed, rolled moisture dry, coated with graphite, screened, blended and packed out. Wastewaters consist of the two washes, plus cooling water from solvent distillation. The wash and screening waters pass through separate clarifiers, where settleable solids are removed. The clarifiers overflow to an industrial waste sewer, which discharges a variety of plant wastes into a series of three shallow lagoons (1a(3)). All cooling water is recycled through a cooling tower (3a). Approximately half of the process water use is in the wet screening operation (3a). Process water use is summarized in Table 46. Wet screen sizing accounts for over half of the total process water use, with wash water representing an additional major fraction. The wash water is heavily contaminated with collagen, benzene and sodium sulfate (3a). Detailed waste characterization data are not available on the ball powder process effluents (3a). Solvent levels in selected effluents are given in Table 47. The ball still effluent, due to its high solvent concentration, and the wash water, due to its large volume, account for most of the solvent discharge for the ball powder processes. In addition to solvents the presence of collagen presents a major problem due to its high BOD, and foaming characteristics (3h).

Table 45. Characteristics of Solvent Recovery Still Bottoms at Radford, (1n(3)) and Badger (1a(3)) AAP's

Parameter*	Radford-Bldg 1502		Radford-Bldg 1503		Badger	
	Range	Average	Range	Average	Range	Average
Temperature, ^{o}F	-	-	-	-	57-7120	110
pH	6.7-7.4	7.1	6.5-9.0	7.4	6.0-11.5	9.0
Total Solids	25-98	49.7	4060-5997	5146.7	612-4639	1885.0
Suspended Solids	3-12	7.2	2264-2545	2451.3	40.9-427	251.0
TOC	15-40	29.7	500-1240	824.3	31-1160	516.8
COD	32-144	104.0	3400-3640	3520.0	48-1560	347.2
BOD_5	24-78	44.7	1850-3500	295.0	-	-
NO_2 + NO_3-Nitrogen	-	3.0	-	-	2-425	143.7

*All parameters except temperature and pH in mg/1.

Table 46. Process Water Use in Ball Powder Manufacture (3a)

Process	Volume, gpd	Percent of Total
NC Storage Pits	101,856	3.3
NC Grinding	164,475	5.3
Extraction	170,163	5.5
Weighing	108,398	3.5
Ball Still	109,626	3.5
Washing	591,752	19.0
Wet Screening	1,728,000	55.7
Coating	87,290	2.8
Roll and Dewater	9,094	0.3
Miscellaneous	34,272	1.1
Total(1)	3,104,926	100.0

(1) Represents approximately 30 percent of full-scale production of ball powder.

Table 47. Solvent Levels in Selected Ball Powder Process Effluents (31)

Process	Ethyl Acetate, mg/l	Ether, mg/l	Benzene, mg/l
Grinding	-	31.5-69.6	-
Extraction	12.0-36.2	2.4-5.6	5.1-16.7
Ball Still	140.5-1942.0	-	0.1-12.1
Washing	35.5-93.4	-	< 1.0
Coating	0.1-18.1	-	0.04-0.4

67. Effects of Water Management

a. Several opportunities exist for effective water management in the manufacture of solvent propellants. Some, such as the complete recycle of cooling water for ball powder manufacture at Badger AAP, have already been implemented. At Radford AAP, dry sweeping of propellant manufacturing buildings is employed prior to washdown, to reduce propellant loss through washdown (1n(3)).

b. Recycle of cooling water from solvent rectification at Radford AAP provides an opportunity for significant water savings. This water, used for cooling of the solvent recovery stills, is uncontaminated and could be reused in another area or recycled through a cooling tower (6e). Cooling water totals about 0.43 MGD from the rectification unit at Radford (1n(3)). Further the hot water-dry wastewater, used to flush residual solvent from cut propellant prior to final gas purging, can be recycled and reused. Preliminary studies at Radford AAP indicate that this process water may be recycled 9 to 14 times before becoming excessively contaminated with solvent (6a). At this point, it would appear feasible to recover solvent from the water-dry waste by distillation, and possibly to continue to recycle the water.

c. Propellant conveyance water (Table 44) averages 0.21 MGD at Radford AAP. This water is relatively uncontaminated, and could possibly be continuously recycled.

d. In the clean-up of screens, dies and other metal objects used for propellant manufacture, the metal parts are first cleaned in hot concentrated caustic, followed by rinsing in 500 gallon tanks of wash water. Wastewater discharge from the cleaning operation could be significantly reduced by using the rinse water to make up fresh caustic cleaning solution.

e. Finally, in the manufacture of ball powder at Badger AAP, it has been suggested that process water use could be reduced by more than half, through recycle of the wet screening water (3a). Complete recycle would reduce total wastewater volume from above 3 MGD to less than 1.4 MGD (Table 46).

68. Current Treatment Practice

a. Partial treatment of several process effluents occurs as the result of solvent recovery operations in manufacture of both solvent propellants and ball powder, as previously described. Beyond solvent recovery however, there is little treatment applied to wastewaters from solvent propellant manufacture. At Radford AAP, solvent recovery still bottoms are combined with other plant wastes, and sent to the acid neutralization facility. The still bottoms, however, are already at near-neutral pH (Table 45).

b. Ball powder wash and screening water, after flowing through settleable solids catch tanks, is combined with other plant wastes and discharged into a series of three shallow lagoons. Screened catch tanks are also used at Radford AAP, although they are reported to be ineffective (4c, ln(3)). At NOS Indianhead, press water from NC purchased water-wet is treated in an activated carbon column prior to discharge (15z1). No data are available on the carbon column performance.

c. One commercial explosives manufacturing plant, which produces smokeless (ball) powder plus NG and other intermediates except NC, uses extended aeration activated sludge followed by lagooning to treat the combined waste flow (4d).

d. The activated sludge unit operates with 24 hours aeration at 8000-9000 mg/l mixed liquor suspended solids. There is little excess sludge wasting required for the plant. The lagoon has 5-10 days detention time, and is aerobic to facultative anaerobic, depending upon temperature and waste loading to the lagoon. Table 48 presents operating data on the treatment system.

e. Although only limited data are given for the activated sludge effluent, this process results in BOD_5 removal exceeding 95 percent. Table 48 also summarizes the treatment efficiencies for the activated sludge plus lagoon treatment sequence. Effluent nitrogen levels are below 0.3 mg/l. The effluent from the lagoon is spray irrigated on a four acre field, at 3 inches hydraulic loading per month.

f. Dickerson (16zx) has also reported the use of biological treatment for a smokeless powder explosives waste. Based upon pilot studies, a two-stage trickling filter was employed to treat process effluents ranging up to 4500 mg/l in BOD_5. Operation at hydraulic loadings of 20 MGAD* on both units, with a recycle ratio of 20:1, yielded BOD removal of 97.5 percent and effluent BOD of 90 mg/l. Lower hydraulic loading rates (8-16 MGAD) slightly improved treatment efficiency, yielding a final effluent BOD of 55 mg/l. However, severe problems were experienced with clogging of the filters at the lower hydraulic loading rates.

69. Modifications to Current Treatment

a. Although preliminary treatment feasibility studies are underway on wastewaters of solvent propellant manufacture, only at Radford AAP are actual modifications in progress (3f). These modifications consist of three projects as follows:

(1) provide open drain guttering and primary solids separation facilities at individual process buildings to remove settleable solids,

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*Million Gallons per Acre Per Day

Table 48. Smokeless Powder Wastewater Treatment Plant Operation and Average Waste Concentration (4d)

Parameter*	Influent	Activated Sludge Effluent	Lagoon Effluent	Percent Removal
pH - Range	6.5-8.8	7.4-8.4	7.5-10.5	-
Total Solids	1646	-	1137	30.9
Suspended Solids	292	-	47	83.9
BOD_5	628.0	29.2	16.8	97.3
COD	1175	117	114	90.3
BOD_5/COD	0.53	0.16	0.15	-
Phosphorus	0.28	-	0.15	46.4
Chlorides	97.0	-	107.1	-
Oil and Grease	35.0	-	8.0	77.1
Ammonia-N	-	-	0.25	-
Kjeldahl-N	-	-	0.17	-
Nitrate-N	-	-	0.04	-
Nitrite-N	-	-	0.1	-
Sulfate	351.4	-	76.6	78.2

*All concentrations in mg/1, except pH.

(2) A sewer system consisting of existing and new sewer lines to carry the wastewater to a proposed activated sludge secondary treatment facility. Separate sewer systems will be provided for uncontaminated cooling water and storm water runoff.

(3) the proposed secondary treatment facility, which will have a capacity to treat 3 MGD of combined wastewater.

b. The activated sludge process, based upon experience at the commercial explosives plant described above (4d), should provide effective removal of organic solvents and other biodegradable constituents. There is some limited data however to indicate that the water-dry waste is stimulatory to filamentous bacteria, which may develop in the activated sludge process (16zw). If a significant population of filamentous organisms does develop, a condition called "bulking" occurs in which the activated sludge will not settle in the secondary clarifier. The sludge floc then carries over the clarifier weir, resulting in deterioration of effluent quality, and inability to sustain an acceptable microbial population in the activated sludge process. The effectiveness of the activated sludge process in removing soluble NC is unknown, although removal of NC fines carried over from the proposed catch tanks should be effective. Removal of particulate explosive is likely to be by entrapment of the particulate material in the activated sludge floc.

c. Radford AAP has proposed treatment for the spent caustic solution used to clean screens, dies and other metal objects which have come into contact with propellant (6a). The proposed treatment involves installation of a neutralization task, where the spent caustic solution will be treated with concentrated sulfuric acid. The neutralized waste will then be hauled by tank truck to a proposed waste propellant incinerator. This treatment process is to be implemented only if the red water, into which the caustic is now blended, can no longer be sold (6a).

70. Alternatives to Current Practice

a. Major sources of pollutant discharge from solvent propellant manufacture include the solvent recovery and water dry operations. These wastes are high in both solvents and dissolved organic propellants. Numerous methods have been proposed to treat the solvents contained in the solvent recovery and water dry wastes. These methods include biological treatment, air stripping, activated carbon absorption, ozonation and reverse osmosis. Reverse osmosis is normally ineffective in removing low molecular weight organics such as solvents from wastewaters. Table 49, which presents results of laboratory scale reverse osmosis treatment of solvent rich waste streams from Radford AAP, confirms the inability of the reverse osmosis process to effectively remove organic solvents. Equally ineffective was ozone oxidation, as shown by the data of Table 50. Ether removal by ozone treatment is attributable primarily to stripping by the ozone gas stream, rather than chemical oxidation (6e).

Table 49. Results of Reverse Osmosis Treatment of Solvent Wastewater (3y)

Constituent	Percent Removal
Alcohol	20
Ether	38
Dinitrotoluene	75.5
Diphenylamine	100
Dibutylphthalate	100
Ethyl Centralite	100
Dimethylphthalate	25
Ammonium Perchlorate	95

Table 50. Ozone Oxidation Treatment of Solvent Wastewater (3y)

Constituent	Percent Removal
Alcohol	33
Ether	100
Dinitrotoluene	38
Diphenylamine	100
Dibutylphthalate	100
Chemical Oxygen Demand	20
Total Organic Carbon	11

b. Laboratory scale air stripping studies on solvent wastes resulted in removal of only 20 percent of the organic carbon within three hours, and 40-45 percent removal during a total of 22 hours of treatment (6e). With the exception of ether, for which air stripping was completely effective within one-half hour, the process does not appear to have applicability to solvent wastes.

c. Biological treatment is capable of removing solvents from the wastewaters (3f, 6a). However, recent activated sludge process treatability studies were only partially successful in treating a water dry waste from Radford AAP (16zw). Treatment of influent BOD_5 concentrations of 176 to 888 mg/l yielded only 65-76 percent BOD removal. Effluent BOD values up to 316 mg/l were observed. Further, the waste was stimulatory to filamentous growth, which normally interfereswith efficient activated sludge process operation. Successful activated sludge treatment of a commercial solvent propellant waste has been reported however, where the solvent propellant waste was mixed with and diluted by other plant process waste streams (4d).

d. One possible beneficial use of solvent wastes may be as organic substrate carbon donors for biodenitrification. Preliminary studies indicate that the organic solvent wastes are effective carbon donors in the biodenitrification process (15y).

e. Activated carbon adsorption appears to provide best solvent removal from solvent recovery and water dry wastes. Complete removal of ethyl alcohol, acetone and diethyl ether, and essentially complete COD removal resulted from carbon treatment of Radford AAP wastewaters (6e). Adsorption capacities on Witco Grade 718 activated carbon for ethyl alcohol, acetone and diethyl ether respectively were 0.82, 1.06 and 1.11 lbs solvent per cubic feet carbon (6e). The effectiveness of carbon treatment suggests the possibility of steam regeneration of the carbon, with solvent recovery and reuse.

f. Carbon is equally effective in removing soluble organic propellant constituents from the wastewater (3y). Results are presented in Table 51, along with results of reverse osmosis and ozone treatment.

g. Solvent rectification still bottoms, although much more concentrated than other solvent wastes, have characteristics and constituents similar to the solvent wastes (Table 45). Based upon the success of activated carbon treatment for both solvent and soluble propellant ingredients of the solvent wastes, still bottoms would likely be best handled by blending with the solvent wastes, and treating the combined flow with activated carbon.

h. The spent caustic cleaning solution, used to clean metal dies and screens, represents a small but highly concentrated waste stream. In addition to the caustic itself, the wastewater contains degradation products of propellant contaminants on the metal parts. The

Table 51. Treatment Results for Dissolved Organic Propellant Ingredients (6e)

Ingredient	Initial Concentration, mg/l	Reverse Osmosis	Ozonation(1)	Activated Carbon
Dinitrotoluene	316	125	230	2.1
Diphenylamine	0.9	0.9	0.0	0.0
Dibutylphthalate	0.17	0.0	0.0	0.08

(1) Seventy-five minute ozone treatment.

waste contains essentially only soluble constituents, which are neither amenable to physical nor biological treatment (3f, 6a). As discussed in prior sections of this chapter, the propellant constituents are also not effectively treated by chemical means. In the absence of availability of treatment methods, the problem of this waste seems best handled by seeking an alternate metal cleaning technique, which either results in no waste effluent, or yields one susceptible to treatment. One alternate technique which appears promising is the substitution of the hot caustic with an organic solvent. This cleaning system may permit recovery of both the cleaning media and the propellants. Organic solvents which have proven successful in cleaning the metal parts within less than one hour contact and at ambient temperature include methanol, tetrahydrofuran, acetone, benzene and ethyl acetate (15zp). In acetone, the most effective solvent, NC concentrations up to 2 percent do not interfere with cleaning efficiency. Above this concentration, cleaning rate declines rapidly (31). Substitution of solvent for caustic cleaning will eliminate discharge of spent caustic contaminated with propellant, and possibly allow recovery of propellant plus recycle of solvent.

i. Various physical and chemical techniques have been attempted to treat the collagen wastes associated with ball powder manufacture. Coagulation, chlorine oxidation, aeration and steam stripping have all been attempted with only limited success (16zx). Best and most consistent results have been achieved by biological treatment, including both activated sludge (4d, 16zx) and trickling filtration (3h, 15y, 16zx). However, Badger AAP has tested the trickling filtration process for treatment of collagen waste, and found that the present trickling filter at the plant lacks adequate treatment capacity for the collagen wastewater volumes associated with full mobilization. Installation of an activated sludge treatment system has been recommended (9c).

71. Summary

a. Volumes of wastewater associated with solvent propellant manufacture are relatively small compared to effluents of most other explosives and propellants. The wastes, however, are high in organic solvents and dissolved propellant constituents. Inadequate wastewater characterization data are available on either waste volumes or wastewater constituents, and an effort to better characterize the wastes is warranted.

b. Wastes are typically not treated prior to discharge, with the limited exception of some partial pH adjustment. There appears to be a significant potential for application of water management techniques leading to reduced water use, wastewater recycle and product recovery, although some residual waste volume would still remain to be treated.

c. Some effort, largely unsuccessful, has been directed toward treatment for solvents removal from wastewaters such as the "water dry" waste. Among the many methods assessed, only activated carbon and biological treatment appear to be both effective and reliable. Biological treatment is currently employed at one commercial explosives plant, and has been proposed for both Radford and Badger AAP's. While probably effective for solvent degradation, the possibility of biotransformation of waste propellant constituents into even more undesirable compounds cannot be ignored. The propensity of many plants to propose biological treatment reflects only economic factors and, until the possibility of biotransformations has been more thoroughly explored the use of biological treatment should be viewed with caution.

SECTION VIII-B - SOLVENTLESS PROPELLANTS

72. Introduction

Solventless propellants are used to make mortar increments and some extruded rocket motors. Rocket motors are manufactured at NOS Indianhead and Badger and Radford AAP's. The latter AAP also makes mortar increments.

73. Waste Sources

a. Solventless propellant (rolled powder) is prepared in a batch process in which chopped NC, NG and various sensitizers and inhibitors are slurried in water, centrifuged to a wet cake, and dried to a paste. After blending, the mixture is rolled into homogeneous plastic sheets. These sheets are then slit to width, and made into "carpet rolls." The carpet rolls are extruded in a hot press to form solid rocket motors. The extrusions are cut to length, dried and cured, and then trimmed to required dimension on a lathe. For mortar increments, the rolled sheets are sewed together, die cut and punched.

b. The specific processing steps of solventless propellant manufacture are as follows (6e):

(1) NC, NG and other constituents including a lead salt are first premixed. Water is used only for building and equipment clean up.

(2) The premix is transferred to another operation where water is added to form the slurry. This slurry is centrifuged. The centrate is recycled back to the slurry mix, for reuse. The water is discharged only when the propellant formulation is changed.

(3) The centrifuged propellant is then tumbled to blend and partially dried to a paste, which is fed to rollers. Water use results from clean up, dust control processes and automatic sprinkler fire systems upon accidental firing of propellant on the rollers.

(4) The rolled propellant is then extruded into solid rocket motors or sewed and cut into mortar increments. Water use results from clean up, cooling, and chip removal from machining and sawing operations.

Table 52 presents wastewater characterization data for the various processing steps at Radford AAP. All wastewaters are notably high in NG, with the slurry mix wastewater containing 1500 mg/l NG plus 800 mg/l DNG. Lead is also high in this waste, up to 300 mg/l as is organic material (BOD, COD, TOC), nitrate and dissolved solids. The Premix Blender and Machining clean-up waters contain more moderate levels of pollutants,

Table 52. Wastewater Characteristics from Solventless Propellant Manufacture at Radford AAP (6e)

Constituent	Premix	Slurry Mix	Blender	Rolling(2)	Rolling(2) Cleanup	Machining
pH	8.3	6.4	7.0	8.9	10.4	7.2
BOD	22	680	-	-	-	-
COD	91	3526	31.7	31	197	59
TOC	27	1081	10	13	137	-
Nitrate	3.2	177	6.8	6.9	-	14.8
Suspended Solids	45	13	2.4	6.9	179	1.9
Dissolved Solids	393	1117	74	462	1582	96
Nitroglycerin	20	1500	21	10	7.3	15
Dinitroglycerin	-	800	-	-	-	-
Lead	0.7	0-300	0.5	-	0.3	-
Flow, gpd	200	1500	45,000	85,000	7200	30,000

(1) All values except pH and flow in mg/1. Values reported are averages.

(2) Values reported for "Rolling" represent normal total flow. Values reported for "Rolling Clean up" represent major clean up water only.

while the Rolling clean up water is high in organics, nitrate, and solids. The high organic and solids content of the Rolling clean-up water is reported due to the use during clean up of asbestos plus cleaning compounds (1n(3)). Solventless propellant manufacture at Radford AAP is reported to result in a total wastewater discharge of 3 MGD (3f). Of this, a significant fraction is cooling water. Waste characterization data are not available for Badger AAP or NOS Indianhead. At Badger AAP, as a result of separation of process from cooling water, and implementation of various water management techniques described below, the process flow is of small enough quantity to dispose to a evaporation/percolation pond, from which there is no overflow (1a(3)). Wastewater volumes are presented in Table 53. Above 88% of the total water is related to cooling use.

74. Effects of Water Management

At Radford AAP, centrate slurry water is recycled back to the slurry mix tank, significantly reducing the discharge of NG and other constituents shown in Table 52. The water is discharged to waste only upon a change in propellant formulation (6e).

An extensive water management program has been implemented at Badger AAP (3a). Procedural changes have resulted in a 50% reduction in water consumption in the Paste Area and further reductions are possible, primarily in cooling water reuse by recycle (3a). At Badger AAP, almost all process water is recycled, with the exception of the dowel and spiral wrap flush and clean up water (Table 53). This process flow represents 988,520 gallons/month. Cooling water from the Roll and Press Area totals 3.9 million gallons per month and from the Paste Area about 7.6 million gallons per month. This latter flow has been reduced approximately 50% by elimination of cooling water use in winter to prevent drain line freeze up, and by reducing flow rate during other periods of operation (3a).

75. Current Treatment Practice

a. At present, solventless propellant wastewater treatment at Radford AAP is restricted to catch tanks, to remove readily settleable suspended solids. Catch tank effluents are discharged without further treatment. From the data of Table 52 most pollutants of the wastewater are in soluble form. Hence, the existing catch basins appear to be of limited utility (1n(3)).

b. At Radford AAP, a new wastewater collection and treatment system has been programmed (3f). This will include combined collection of process wastewater with cooling and storm water, primary settleable solids removal, and secondary treatment by processes which have not yet been specified (3f). Pilot studies on biological treatment are currently underway (15zp).

Table 53. Badger AAP Rocket Area Water Usage (3a)

Area	Use of Water	Gallons/Month
Paste	Tank Wash	25,700
	Wet Floors	216,720
	Cooling (Hydraulic System)	3,696,700
Total		3,939,120
Roll and Press	Wash Down	167,000
	Cooling (Vacuum System)	604,800
	Cooling (Hydraulic System)	3,316,320
Total		4,088,120
Finishing	Dowel and Spiral Wrap Flush	604,800
Total		604,800
TOTAL USAGE		8,632,080

c. At Badger AAP, process wastewaters are screened to remove propellant chips and flakes. The screened effluent, which contains smaller particles of solid propellant, discharges through baffled ditches to a closed pond (1a(3)). Baffling enhances the sedimentation of suspended solids in the ditches, which are periodically cleaned out. The wastewater in the pond is lost through evaporation and leaching. The pond is reported to overflow only during periods of intensive rainfall (1a(3)). Except during these periods, there is no discharge of process wastewater for Badger AAP solventless propellant manufacture.

76. Alternatives to Current Practice

a. The primary constituents of concern in solventless propellant process wastewater are organics including nitroglycerin and dinitroglycerin, nitrate, suspended solids including solid propellant, and lead. With the exception of lead, treatment alternatives for the other constituents have been assessed in preceding sections of this chapter.

b. Lead may be removed by a variety of processes, including hydroxide or sulfide precipitation and ion exchange, the two most effective and widely used techniques (16zy). Lead levels in Radford AAP wastewaters of up to 300 mg/l have been reported (6e), although most process effluents contain sub-mg/l levels (Table 52). At lead concentrations below 5 mg/l, and particularly for large volume flows, hydroxide precipitation treatment is relatively ineffective and uneconomical (16zy). Therefore, ion exchange treatment appears to be most directly applicable to lead bearing wastewaters from solventless propellant manufacture. Ion exchange or sulfide precipitation has the further advantage of possible recovery of the lead upon regeneration of spent resin.

c. Preliminary studies on ion exchange treatment of solventless propellant slurry mix water have indicated that while several resins have limited efficiency, Duolite ES 63 resin is capable of reducing lead to about 0.01 mg/l, at flow rates up to 2.7 gal/min/cubic feet of resin. At higher flow rates, treatment efficiency drops off rapidly. Although saturation capacity of this resin for lead exceeds 3 lb./cu. ft., significant lead leakage occurs above a loading of 2 lb. lead/cu. ft. of resin (6a).

77. Impact of Air Pollution Control

Currently, a portion of the Radford AAP wastewater from the solventless propellant blending area is air pollution dust scrubber water from rotoclones (1n(3)). It is proposed to partially recycle this scrubber water (3u), with overflow discharges to the proposed main plant treatment system (6a).

78. Summary

a. Wastewaters from solventless propellant production result primarily from building clean-up and equipment washdown. According to characterization data for Radford AAP, the wastewaters are high in BOD, nitrate, suspended solids, NG and DNG, and lead. With the exception of Badger AAP, these wastes are discharged without treatment. Except for lead all constituents are, however, treatable as described in previous sections of this chapter. Through implementation of several water management techniques, Badger AAP has sufficiently reduced process waste volume to allow utilization of percolation/evaporation ponds. Although there are possible questions concerning the possible contamination of soil and ground water from leaching of propellant wastewater, the water management program implemented by Badger AAP has been effective in itself, and appropriate elements of this program should also be implemented at Radford AAP.

b. Although pilot biological treatability studies are to be undertaken at Radford AAP, caution is indicated in the face of current lack of knowledge of possible biotransformation of propellant wastewater constituents into environmentally unacceptable compounds. In any event, biological treatment is ineffective for lead control, although other treatment technologies are available. Among these processes, ion exchange appears to offer most promise.

SECTION IX - MISCELLANEOUS LAP ACTIVITIES

79. Introduction

The three major load and pack operations at military munition plants are: the casting of melt-pour explosives; the casting of plastic-bonded explosives; and the casting of composite propellants into solid rocket motors. All operations involve processing steps for intermediates.

a. Major wastewater constituents associated with LAP casting of melt-pour explosives are discussed in Section II (Trinitrotoluene) and Section V (RDX and HMX) of this chapter.

b. This section is devoted primarily to: wastewaters from casting of composite propellants; wastewaters associated with processing of secondary ingredients of pressed explosives; and casting of plastic bonded explosives.

SECTION IX-A - CAST PROPELLANTS

80. Introduction

a. Cast propellants are so identified because slurry-propellant formulation is either poured directly in the rocket case (composite propellant) or formulation blended "in-place," (composite double-base propellant) followed by curing to form a solid rocket motor. Most large rocket motors are cast. Smaller motors are typically extruded, as described in Section VIII. There are exceptions, such as the small TOW motor, which is cast in plastic forms at Radford AAP (6a).

b. Rocket motors may be cast from either fine NC-base casting powder with NG added to form a double base, or from aluminum powder oxidizer, and other ingredients stabilized in a polymer binder such as polybutadiene or polybutene. Both types of casting formulations include trace amounts of catalysts and stabilizers in addition to typical oxidizers such as ammonium perchlorate or HMX oxidizer.

c. For the polymer based motor, ingredients including ammonium perchlorate are pre-mixed and blended in large kettles to form a slurry. A polymer cross-linking agent is added just prior to completion of mixing, and propellant slurry is poured into the rocket case. Upon curing, the slurry solidifies into a rocket motor. In casting the double base propellant, casting powder is loaded into the rocket case, and acetone plus NG added to dissolve the powder. Nitrogen or dry air is bubbled through the mixture to remove the acetone, and yield a dense gel. The loaded rocket is then cured in an oven, during which the gel solidifies.

81. Waste Sources

a. Wastewaters are associated with dust abatement procedures, and equipment and building clean-up. Typically, water use is minimized in the actual vicinity of propellant casting operations, as moisture is detrimental to propellant quality (15zm). Wastewaters from dust abatement result from grinding of ammonium perchlorate and HMX. No characterization data are available on either dust abatement or clean-up wastewaters. Double-base propellants are cast in closed systems and are thus not generally subject to polluting wastewaters. Because of the small volumes of wastewater involved, and the widespread use of evaporation ponds for final disposal, there is little activity or need in water management and recycle.

b. Size reduction is required for both ammonium perchlorate and HMX where used in composite and double-base propellants. Prior to blending these oxidizers into the propellant, size reduction is accomplished in hammer mills, with size control by screening. Sized oxidizer is then sent to the blending operation by either forced air conveyers, or preweighed and transported in containers. At Radford AAP, dust from the grinding and weighing operations is removed by a duct system to a wet scrubber. The flow from the scrubber is discharged without treatment. A dry-type dust collection system has been proposed, with the collected dust incinerated (6a).

c. Both Air Force Plant #78 and NAVPRO Magna grind HMX. At Magna, dust is vented to a wet scrubber system (15zj). Overflow, plus HMX equipment and process building washwater is discharged through catch tanks to earthen sumps. The sumps are allowed to dry up by evaporation (annual evaporative rate of 56 inches/yr.), and the dried residue burned. At some process points, catch basins are preceded by nylon filter bags to enhance solid HMX removal (15zj). AF #78 uses air prefilters plus a hospital-type "Absolute Filter" (American Air Filter Co.) to control HMX grinding dust (15zk). This filter system removes particles down to 0.3 microns in size. Building and equipment washwater is discharged into a collection pit, and transferred to an evaporation pond. The pond residue is burned (15zk).

d. Many LAP plants grind ammonium perchlorate. Both AF #78 and NAVPRO Magna have dry dust control systems for the grinding operations (15zj, 15zk). The Magna grinding equipment is totally enclosed, and there is no escape of dust. AF #78 uses a baghouse control system. Both plants, however, use water clean-up of the grinding equipment and buildings. At AF #78, washwater is collected in concrete lined sumps. When the sumps are filled, the contents are transferred to evaporation pits, where the residue is burned (15zk). Magna uses a similar system of catch tanks and evaporative ponds.

e. Other LAP plants grinding ammonium perchlorate typically use wet scrubber systems for dust control. At Longhorn AAP, vacuum ducts exhaust dust laden air to a wet scrubber. The scrubber bath is stagnant, with bath contents dumped once per shift to a collection sump. Sump contents are transported by truck to a large evaporative pond (15zm). Clean-up water is discharged by surface ditches to a large lake located on the plant property. Ammonium perchlorate transport containers are washed, with washwater stored in a 35,000 gallon tank and bled to surface drainage when surface flow is sufficient to provide dilution (3f).

f. Redstone Arsenal has a wet scrubber system for ammonium perchlorate grinding dust control (15zo). Scrubber water is shipped in drums to the scrap propellant burning ground for disposal. Building and equipment washdown water discharges through sumps to creeks. Due to the high water solubility of ammonium perchlorate, sumps would be ineffective in controlling discharge of the oxidizer. At the Aerojet Sacramento plant, a similar system is used for dust control. Ammonium perchlorate grinding dust is removed by wet scrubbing. Scrubber water is retained in a holding pond, and recirculated. The ammonium perchlorate grinding and conveyance systems are designed to prevent dust escape and thereby avoid building and equipment washdown, and as a result there is no clean-up water associated with this process (15zm). Both Redstone and Aerojet transport ground ammonium perchlorate by forced air conveyance systems (15zm, 15zo). Conveyer air is recirculated at Aerojet (15zm), while Redstone exhausts the air through baghouse collectors (15zo).

g. Clean-up of propellant handling equipment such as slurry kettles, and propellant loading buildings, is normally by a routine of dry hand cleaning, followed by solvent cleaning and final wash with soapy water. At NAVPRO Magna, any floor spills are scraped and hand-wiped by freon-damp rags. This is followed by an acetone wipe, and a soap and water wash (15zj). Floors are also cleaned in this manner at the end of each shift. Soapy water discharges through catch tanks into evaporation pits. The presence of any solid propellant in the catch tank results in a special investigation by plant management. Typically the wastewater is soapy wash water, with traces of acetone (15zj). Equipment is cleaned by scraping, freon wiping and acetone wash. Water is normally not used.

h. AF #78 first washes buildings and equipment with a high pressure water jet, followed by hand wiping with methyl chloroform. Water is collected in concrete lined sumps, and transported by tank trucks to evaporative ponds (15zk). The water is evaporated, and residue burned. Aerojet (Sacramento) uses no water at all in building clean-up. Cleaning is by dry and solvent processes only (15zm). Casting bowls, mixers and other equipment are cleaned by wiping with trichlorethane followed by a water wash. Solvent is collected in concrete sumps and disposed by burning. Water is discharged to evaporation ponds (15zm). Redstone Arsenal uses a combination of solvents plus detergents and water for equipment and building clean-up. Wash waters discharge through catch sumps to surface drainage (15zo). Equipment clean-up water is partially recirculated. All of the above approaches appear to be effective.

SECTION IX-B - PRESSED EXPLOSIVES

82. Introduction

Secondary ingredients of pressed explosives which impact on process water quality at LAP facilities are primarily powdered aluminum, and ammonium picrate (Explosive "D"). Powdered aluminum is used in a variety of pressed explosives, including HBX-1 (NAD Hawthorne), H-6 (NAD Crane, NWS Yorktown), Tritonal (NAD Crane, NWS Yorktown, NAD McAlester, NAD Hawthorne), Minol (NAD McAlester), and other composition explosives. Ammonium picrate is used in Picratol formulation, a blend of TNT and Explosive "D". Other significant explosives, used in detonators, are lead azide and lead styphnate. Lead azide is no longer manufactured. The Army is investigating methods to destroy lead azide (3h).

83. Waste Sources

a. Aluminum is received at LAP plants in powdered form, and processing is limitedto screening, weighing, transporting and blending with the composite explosive mixture. Wastewaters associated with powdered aluminum result from dust abatement and building and equipment clean-up. No characterization data are available on these wastewaters. Many plants exhaust aluminum dust directly to the atmosphere, without dust control. Others use wet scrubbers. Plants without dust control plan to incorporate scrubber systems, and handle the scrubber water in a variety of ways. NAD McAlester will use an overflow lagoon (15za). Since aluminum is relatively insoluble, most scrubbed aluminum would be expected to remain in particulate form, and unless solids removal occurs in the lagoon, aluminum will be present in the lagoon discharge.

b. NWS Yorktown currently uses a wet scrubber system for powdered aluminum dust control (15zh). Wet scrubbing was selected in preference to dry collection and recovery, due to the possibility of explosive hazard (14r). Scrubber overflow discharges to baffled sumps, and thence to surface drainage (15zh). Sumps are mucked out weekly, with sludge burned. In contrast to the Yorktown system, NAD Hawthorne successfully uses a dry cyclone type dust separator for their aluminum sieving operation (15zc).

c. Ammonium picrate is used at NWS Yorktown, and NAD Crane and Hawthorne, to formulate Picratol, which contains approximately half TNT and half ammonium picrate (14zb). Process wastewaters from Picratol manufacture are currently discharged through catch basins to surface drainage (15ze, 15zh, 14zb). At NWS Yorktown, however, Picratol dust is vented to a dry collection system (14r).

84. Treatment Practice

a. Various treatment methods have been assessed for ammonium picrate wastewater. Biological degradation is not effective (15ze, 16o).

A comprehensive pilot study of physical-chemical treatment processes for Picratol wastewaters, carried out at NAD Hawthorne, indicated that activated carbon adsorption is most consistently effective (14zb). Treatment results are presented in Table 54.

b. There is effectively no information on the wastewater characteristics or treatability of wastewaters associated with lead styphnate use. Wastewaters originate from building and equipment washdown, and dust scrubber systems. At Kansas AAP, the wastewater is retained in holding pits, where it is treated with caustic to "kill" the lead styphnate (1h(3)). The wastewater is then discharged to holding ponds. The pH of the caustic-treated wastewater is unknown. Although some lead hydroxide precipitate may be removed in the treatment process, most effective treatment by lead precipitation occurs near pH 10, with lead being significantly more soluble at higher or lower pH (16zz).

Table 54. Pilot Plant Treatment of Ammonium Picrate (14zb)

Treatment Process	Concentration, mg/l		Percent Removal
	Influent	Effluent	
Air Flotation	86	52	39.5
	419	413	1.5
Sand Filter	86	57	33.7
	419	414	1.1
Activated Carbon	86	< 1	98.8+
	419	< 1	99.8+
Polymeric Resin	86	< 1-17	80.2-99.8+
	419	27-270	35.6-93.6

SECTION IX-C - PLASTIC BONDED EXPLOSIVE

85. Introduction

The production of plastic bonded explosives (PBX) is a relatively small experimental operation, compared to production of other military explosives. Currently PBX is loaded at NWS Yorktown (14z). As with cast propellants, solvents are used in the formulation and loading of PBX. At Yorktown, these solvents are collected separately and disposed of by incineration. Solvent- and explosive-contaminated wastewaters are discharged to surface drainage. No characterization data are available on these wastewaters. No treatment system has been proposed for these wastes at present (14z), although the U. S. Navy is conducting research programs to develop water-soluble and other binders more amenable to pollution-free disposal (15zr).

86. Summary

There is sparse information available on wastewater volumes or characteristics of the minor LAP activities discussed in this section. In general, such wastewaters originate from air pollution abatement, and building and equipment clean-up procedures, and presumably reflect the constituents of the loaded explosives and propellants. Despite widespread LAP activities, little effort seems to be currently directed toward either waste characterization or treatment of the wastes described in this section. A waste characterization program is indicated, in order that treatment needs for these minor LAP facilities can be defined, and effluent criteria established.

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